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REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS. 1908.

Received November 6, 1907.

Since the preparation of our report for 1907, several important determinations of atomic weights have been published. They are, briefly, as follows:

Nitrogen.—Richards and Forbes[1] have redetermined the ratio between Ag and NO_3, as shown in the composition of silver nitrate. The ratio found, with all corrections applied, is $Ag:NO_3 = 100:57.479$. Hence, if Ag = 107.930, N = 14.037; and if N = 14.008, Ag = 107.880. In short, the higher atomic weight hitherto assigned to silver is inconsistent with the lower value for nitrogen as found in several recent investigations.

Sulphur.—Richards and Jones[2] have measured the ratio between Ag_2SO_4 and AgCl. From the data obtained, if Ag = 107.930, S = 32.113, a value much higher than that commonly accepted. If Ag = 107.880, then S = 32.069, which is near the figure given in our former tables. Additional evidence relative to this constant is much to be desired, for it influences the determination of many other atomic weights, especially those of the rare-earth metals.

Potassium.—From the ratios Ag:KCl and AgCl:KCl, Richards and Staehler[3] find K = 39.114, when Ag = 107.930 and Cl = 35.473. From the corresponding bromide ratios, with Br = 79.953, Richards and Mueller[4] find K = 39.1143 and 39.1135. The final result of both researches is K = 39.114, a distinct lowering of the constant in question.

Manganese.—Atomic weight redetermined by Baxter and Hines,[5] from

[1] This Journal, 29, 808; and Z. anorg. Chem., 55, 34.
[2] This Journal, 29, 826; and Z. anorg. Chem., 55, 72.
[3] This Journal, 29, 623; and Ber., 39, 3611.
[4] This Journal, 29, 639; and Z. anorg. Chem.. 53, 423.
[5] This Journal, 28, 1560; and Z. anorg. Chem., 51, 202.

analyses of the chloride and bromide. The mean of their very concordant determinations is Mn = 54.957, when Ag = 107.930.

Cobalt.—From new analyses of the chloride, Baxter and Coffin[1] find Co = 58.997, or 59 in round numbers. This confirms the earlier determinations by Richards and Baxter.

Indium.—Mathers,[2] from analyses of indium chloride, found In = 114.88. From the bromide, In = 114.86. The author recommends the adoption of the rounded-off value, 114.9, when Ag = 107.93, Cl = 35.473, and Br = 79.953.

Tellurium.—Norris,[3] by twelve concordant reductions of the basic nitrate, $2TeO_2.HNO_3$ to TeO_2, found the atomic weight of tellurium to be 127.48, when N = 14.01. With N = 14.04, Te = 127.64, which is in better agreement with other recent determinations. The true cause of the difference is not clear.

Neodymium.—Holmberg[4] has redetermined the atomic weight of this element by synthesis of the sulphate from the oxide. In mean, when S = 32.06, Nd = 144.08. This is higher by 0.48 than the value given in our table.

Dysprosium.—In two series of determinations, based upon the ignition to oxide of the octohydrated sulphate, Urbain and Demenitroux[5] find for the atomic weight of dysprosium, values ranging between 162.29 and 162.75. In mean, Dy = 162.53.

Radium.—Madame Curie,[6] in a series of three new determinations, has found a more precise value for the atomic weight of radium. Working with material more abundant and pure than that formerly analyzed, she found Ra = 226.18 when Ag = 107.8 and Cl = 35.4. With Ag = 107.93 and Cl = 35.45, Ra = 226.45. This number is higher than her earlier determination by more than a unit.

From the data here given, and from those cited in previous reports, it is evident that the entire table of atomic weights is in need of revision. The values assigned to K and Na are too high; those given to Cl and S are too low; and these constants affect the determinations of many others. They depend, however, upon the atomic weight of silver, which is probably, but not certainly, as low as 107.88. It is well known that work upon these fundamental constants is now nearing completion in several laboratories, notably under T. W. Richards, W. A. Noyes, and probably other investigators also. Within a few months it should be possible to

[1] This Journal, 28, 1580; and Z. anorg. Chem., 51, 171.

[2] This Journal, 29, 485; and Ber., 40, 1220.

[3] This Journal, 28, 1675.

[4] Z. anorg. Chem., 53, 83.

[5] Compt. rend., 143, 598.

[6] Ibid., 145, 422. The atomic weight of radium is also under investigation by Thorpe.

enter upon a satisfactory revision of the table, a task which would be unsatisfactory, if undertaken now. It is true, as Brauner has suggested,[1] that the present table contains inconsistencies, but they are small in amount, and are due to inconsistencies in the original data from which the values are derived. In our next report we hope to recompute the entire table; but meanwhile, awaiting the completion of the researches which we know to be in progress, we prefer to leave the table practically

International Atomic Weights. 1908.

Aluminum	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	143.6
Argon	A	39.9	Neon	Ne	20.
Arsenic	As	75.0	Nickel	Ni	58.7
Barium	Ba	137.4	Nitrogen	N	14.01
Bismuth	Bi	208.0	Osmium	Os	191.0
Boron	B	11.0	Oxygen	O	16.00
Bromine	Br	79.96	Palladium	Pd	106.5
Cadmium	Cd	112.4	Phosphorus	P	31.0
Caesium	Cs	132.9	Platinum	Pt	194.8
Calcium	Ca	40.1	Potassium	K	39.15
Carbon	C	12.00	Praseodymium	Pr	140.5
Cerium	Ce	140.25	Radium	Ra	225.
Chlorine	Cl	35.45	Rhodium	Rh	103.0
Chromium	Cr	52.1	Rubidium	Rb	85.5
Cobalt	Co	59.0	Ruthenium	Ru	101.7
Columbium	Cb	94.	Samarium	Sa	150.3
Copper	Cu	63.6	Scandium	Sc	44.1
Dysprosium	Dy	162.5	Selenium	Se	79.2
Erbium	Er	166.	Silicon	Si	28.4
Europium	Eu	152.	Silver	Ag	107.93
Fluorine	F	19.0	Sodium	Na	23.05
Gadolinium	Gd	156.	Strontium	Sr	87.6
Gallium	Ga	70.0	Sulphur	S	32.06
Germanium	Ge	72.5	Tantalum	Ta	181.
Glucinum	Gl	9.1	Tellurium	Te	127.6
Gold	Au	197.2	Terbium	Tb	159.2
Helium	He	4.0	Thallium	Tl	204.1
Hydrogen	H	1.008	Thorium	Th	232.5
Indium	In	115.	Thulium	Tm	171.
Iodine	I	126.97	Tin	Sn	119.0
Iridium	Ir	193.0	Titanium	Ti	48.1
Iron	Fe	55.9	Tungsten	W	184.0
Krypton	Kr	81.8	Uranium	U	238.5
Lanthanum	La	138.9	Vanadium	V	51.2
Lead	Pb	206.9	Xenon	Xe	128.
Lithium	Li	7.03	Ytterbium	Yb	173.0
Magnesium	Mg	24.36	Yttrium	Y	89.0
Manganese	Mn	55.0	Zinc	Zn	65.4
Mercury	Hg	200.0	Zirconium	Zr	90.6

[1] Chem.-Ztg., May 11, 1907.

unchanged. A conservative policy seems to be safer than one of haste, and the delay of another year will do no harm. One exception to the rule may, however, be made. Dysprosium, with the atomic weight 162.5, may now be properly added to the list of the chemical elements, and we recommend its insertion in the table.

It is with the deepest regret that we record the loss, by death, in February last, of our distinguished colleague, Professor Moissan. The Chemical Society of Paris has designated Monsieur G. Urbain as his successor upon this Commission.

(Signed)

F. W. CLARKE,
W. OSTWALD,
T. E. THORPE,
G. URBAIN.

THE CHOICE OF THE MOST PROBABLE VALUE FOR AN ATOMIC WEIGHT: THE ATOMIC WEIGHT OF HYDROGEN.[1]

BY WILLIAM A. NOYES.

Received December 6, 1907.

A large amount of material has been accumulated from which the atomic wieghts of the more important elements can be calculated. A very superficial examination of this material reveals the fact that the experimental results on which our knowledge of these constants is based, vary very greatly in their value and that many of the older determinations have been rendered practically worthless by recent work, which has been more careful and accurate.

As some of these new determinations affect the values for elements of such fundamental importance that a recalculation of the whole table of atomic weights will be necessary in the near future, it seems desirable to formulate some general principles to aid in the elimination of results which have little or no value and in the combination of the results which remain. Such principles, if they meet with general acceptance, will be of value, not only for the purpose stated but also as setting a certain standard which must be attained by future workers in this field, if their work is to be of permanent value.

The most important general principle which has been proposed for the combination of the results of different observers, is the one based on the mathematical discussion of accidental errors of observation. In accordance with the theory of probabilities, these results, if subject only to accidental errors, should be weighted in inverse proportion to their

[1] Presented in abstract at the N. Y. Meeting of the American Chemical Society, Dec. 28, 1906.

probable errors.[1] A very serious objection to this method of treatment lies in the fact that every determination of this kind is subject to constant errors, and that the amount of these errors is not proportional to their "probable errors."[2] Thus Stas obtained 132.8445 ±0.0008 parts of silver chloride from 100 parts of silver, while Richards and Wells[3] have obtained 132.8670 ±0.0005 parts. The most probable value calculated by the mathematical rule would be 132.8607. If this value is the true one, the real error of the value obtained by Richards and Wells is 12 times its probable error, while the real error of Stas is 20 times the probable error. And, whatever the true value may be, the real error of one of the results, at least, is many times its "probable error." An examination of other cases shows that the relations here found are typical, and it seems evident that the question of constant errors requires some other treatment than the simple mathematical one. The proper treatment, which is an experimental one, has been clearly illustrated in the case which we have under consideration. Richards and Wells studied their method very carefully with especial reference to the elimination of constant errors and to secure evidence as to the amount of those errors which could not be wholly excluded. They also pointed out certain errors in the work of Stas and determined, approximately, the magnitude of some of these. It is evident for this reason that very much greater weight attaches to the value found by Richards and Wells than to that found by Stas, and it is proposed as a general principle that when a later observer has pointed out sources of error which are considerable in comparison with the "probable errors" and where the later observer has succeeded in avoiding these sources of error, the earlier work must be looked upon as having only confirmatory value and the result of the later work should be accepted without modification. It has been objected to this that the later work is also subject to constant errors which may be in the opposite direction from those of the earlier determination and that if we give a certain weight to the earlier work we may eliminate these errors. But we certainly are not justified in using a value that contains a known error in one direction merely for the chance that we may compensate an unknown error.

[1] F. W. Clarke: "Constants of Nature," Part V., Edition of 1897, p. 7.

[2] Professor Clarke has, of course, recognized the importance of constant errors and has often rejected values which he considers subject to such errors. In 1898 (*Amer. Chem. J.*, **20**, 543) Prof. T. W. Richards pointed out the importance of selecting atomic weights on the basis of the methods employed in their determination and the probable freedom of those methods from constant errors. It is interesting to notice that of the seven values in Professor Richards's table, which differed at that time decidedly from the values given by Professor Clarke, the numbers for four of the atomic weights are nearer to the numbers now given in the International table than were the values then given by Professor Clarke.

[3] This Journal, **27**, 524.

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[3] This Journal, 27, 524.

The principle outlined above has been recently proposed, independently, by Professar Guye,[1] in his discussion of the selection of the most probable value for the density of a gas. A second principle proposed by Professor Guye is that when the values obtained by two observers agree while that obtained by a third observer is discordant, the values which are in agreement should be given much greater weight. As an extension of this principle, a value of an individual worker which differs materially from the values obtained by several others, should be rejected entirely.

After eliminating the results which are excluded by the application of the foregoing principles, it is proposed to arrange those which remain in the order of their probable errors. Any result with a probable error more than five times that of the smallest probable error may be excluded, as such a result will have only one twenty-fifth the weight, according to the theory of probabilities. In practical effect, this is the same as using the mathematical rule which Professor Clarke has so long employed in weighting the results of different workers. As at least five or six observations are necessary to give a probable error which has any significance, results based on a smaller number of determinations may be excluded unless other evidence warrants the belief that the work is of an unusual degree of accuracy.

The values for any given ratio which remain after the elimination of results which have little value, may well be combined by weighting them inversely as the squares of their probable errors.

For further use, the ratios which are selected in this manner should be weighted, not by the probable error calculated by the mathematical rule but by the deviation of the results of different observers from the value selected. If the results of only one observer remain after eliminating untrustworthy values (as in the case of the ratio of silver to silver chloride), this result should be weighted in accordance with the average deviation of the results of this observer from his mean. This will, I think, give a much fairer basis than the "probable error" for weighting the value in such cases. Thus the "mean error" of the value of Richards and Wells given above is 0.0018, while the "probable error" is 0.0005. When we consider the certainty that some sources of constant error will always remain, I think every one will agree that the real error is much more likely to correspond to the former than to the latter value.

After selecting the most trustworthy experimental ratios as suggested, we have still to combine them for the calculation of atomic weights. This may usually be done in a variety of ways. In choosing among these, the same general principles as before should be applied. For a given atomic weight, only those ratios should be used for which the un-

[1] Arch. sci. phys. nat., 24, 44.

certainties of the values will affect the atomic weight chosen less than five times as much as any other combination of ratios which might be used. In most cases this will probably lead to the selection of ratios which furnish a direct comparison with oxygen, silver or one of the halogens rather than of those in which the comparison is more indirect. Densities of gases corrected to the condition of an ideal gas by the method of D. Berthelot[1] may be considered as direct comparisons with oxygen, and molecular and atomic weights calculated from these densities should be included with those determined by chemical methods.

The Atomic Weight of Hydrogen.

The following is a summary of the determinations which have been made of the atomic weight of hydrogen by the chemical method:

	Date.	No. of expts.	Value.	Prob. error.	Real error.	$\frac{\text{Real error}}{\text{Prob. error}}$
Dulong and Berzelius	1821	3	1.00667	356	108	0.3
Leduc	1892	2	1.00749	83	26	0.3
Erdmann and Marchand	1842	8	1.00160	71	615	8.7
Thomsen	1870	8	1.00570	71	205	2.9
Rayleigh	1889	5	1.00692	56	85	1.5
Dumas	1842	19	1 00250	44	525	12.0
Keiser	1898	8	1.00753	31	22	0.7
Dittmar and Henderson	1890	24	1.00840	29	65	2.2
Noyes (recalculated)	1890	24	1.00765	17	10	0.6
Thomsen	1895	21	1.00826	14	51	3.6
Cooke and Richards	1887	16	1.00826	13	51	3.9
Noyes (original)	1890	24	1.00654	11	121	11.0
Keiser	1888	10	1.00306	7	469	67.0
Noyes	1907	48	1.00787	2	12	6.0
Morley	1895	23	1.00762	2	12	6.0

The probable errors of the table are calculated from those assigned by Professor Clarke.[2] For the results of Erdmann and Marchand and Leduc, the values are arbitrary. For convenience these errors are given in units corresponding to the last significant figure of the values for the atomic weights.

On applying the principles which have been outlined, we find that the results of Dulong and Berzelius, Erdmann and Marchand, and of Dumas, are excluded because the later work of Dittmar and Henderson by the same method, demonstrates that serious constant errors were involved in the earlier work. Leduc's value is to be rejected because the number of experiments was too small. Keiser's earlier value is to be rejected because it is not in accord with any of the later work and because he has himself given us a later and better value. My own original value must be rejected because it was subject to a constant error and

[1] Compt. rend., 144, 76.

[2] "Constants of Nature." Part V., p. 24 (1897).

the recalculated result may be considered as superseded by my later and more careful work. Because the probable errors of all of the other determinations are more than five times as great as those of Morley and myself, they would be excluded by the third principle proposed. The final value, if calculated from these two results, is **1.00775.**

It is interesting to notice the relation between the real errors of the various values (assuming this value as true) and the probable errors. *Only in those cases where we now know that there were serious constant errors, is the real error more than six times the probable error.*

Morley calculates a value corresponding to 1.00762 from his determinations of the densities of the gases and their combining volumes. This value has not been considered here, partly because the probable error of the density of hydrogen is about 3 in 100,000, instead of 2 for the chemical method, but chiefly because of the uncertainty of the ratio of the combining volumes.[1]

If a value is calculated by Professor Clarke's method, weighting each result in inverse proportion to its probable error, only Keiser's older value and my own original value would affect the value which I have selected by more than about one part in 100,000. Keiser's older value would, however, reduce it by about 40 parts and my own original value by about 4 parts in 100,000.

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THE RELATION BETWEEN COMPRESSIBILITY, SURFACE TENSION AND OTHER PROPERTIES OF MATERIAL.

(PRELIMINARY PAPER.)

BY THEODORE W. RICHARDS AND J. HOWARD MATHEWS.

Received October 30, 1907.

A recent paper by Albert Ritzel[2] upon gas solubility, compressibility and surface tension, seems to render important the brief publication of some work carried on by us during the winter of 1905–06. This work was presented to the Physico-chemical Club of Boston and Cambridge on May 2, 1906, under the title "The Relation of Compressibility to Other Physical Properties, with Particular Reference to Surface Tension," and was discussed there. On account of the subsequent absence of one of us in Germany the publication of this work has been delayed, the amount of material being so large that a careful study of the relations demanded more time than was then available.

The present notice seems desirable because Ritzel has touched upon one of the relations studied previously by us. He has used the method of determining compressibility which we have used, and shows that this

[1] Morley: "Smithsonian Contribution to Knowledge," No. 980, p. 110 (1895).

[2] Z. physik. Chem., **60**, 319 (1907).

property of substance is a significant one. His paper is interesting and valuable as far as it goes, and scarcely touches at all the immediate ground which we covered, but in order to save the time of any one else who might be thinking of continuing his work, it seems only fair that our results should likewise be put into print.

As Ritzel has referred in his paper to the suggestions of van der Waals and others concerning a possible relation between compressibility and surface tension, it is not necessary for us to repeat this discussion. The subject was studied by us from somewhat a different point of view, namely, from the point of view of the theory of compressible atoms.[1] The logic of our train of thought was this:

Premises.—(1) All bodies under high pressure have a smaller compressibility than the same bodies under low pressure. (2) The physical affinity which causes surface tension probably exerts pressure in its action.

Conclusion.—Therefore, the greater this physical affinity of surface tension, the less will probably be the compressibility under additional outside pressure, at any rate in substances of similiar composition. This probable relationship was suggested by Ostwald at a discussion concerning atomic compressibility in the same Physico-chemical Club in the autumn of 1905, and with his approval we immediately began the study of it. The subject fitted very suitably into the scheme upon which we had already begun work—a scheme which embraced many other physical properties of substance.

In this preliminary notice it is not necessary to describe in detail the methods which we used for determining the various quantities in question. It is enough to say that all the substances were redistilled fractionally until their purity was reasonably satisfactory, the substances of commerce having been shown to be altogether too impure to give significant results. The method of Richards and Stull[2] was used for determining the compressibilities, and with some modifications the method of Ramsay and Shields,[3] for determining the surface tensions; the boiling-points were corrected for the projecting thread of the thermometer, and the specific gravities were determined with great care by means of the Ostwald pycnometer. All the data given below except the heats of vaporization were made in the Harvard Laboratory, some of them as parts of another investigation by one of us in collaboration with Dr. Stull, the rest by the present authors. Each figure is suitably designated in order to show who found it. The heats of vaporization are taken from the work of

[1] Proc. Amer. Acad. Arts and Sciences, 39, 581 (1904); also, Z. physik. Chem., 49, 15 (1904). This Journal, 26, 399.

[2] Z. physik. Chem., 49, 1 (1904); also, Pub. No. 7 Carnegie Institution of Washington.

[3] Z. physik. Chem., 12, 433 (1893).

others, as tabulated in the well-known tables of Landolt and Börnstein. The compressibilities are expressed in terms of the kilograms per square centimeter, which is 0.967 atmosphere; that is to say, a substance having a compressibility of $\beta = 80 \times 10^{-6}$ would be altered in volume by the

Substance.	Compressibility. $\beta \times 10^6$.	Boiling point.	Density 20°/4°.	Surface tension γ.	Vapor pressure at 20°.	Molecular heat of vaporization.	$K = 1000\,\beta\,\gamma^{2/3}$.
Methyl aniline	41.87	195.7°	0.9865	39.46	..	42.67	2.6
Dimethyl aniline	47.98	193.7	0.9555	36.50	..	40.19	2.8
Ethyl aniline	45.89	206.5	0.9625	36.58	..	..	2.6
Diethyl aniline	49.79	217.5	0.9344	34.17	..	..	2.6
Toluidine (ortho)	40.43	196.5	0.9986	39.76	..	42.67	2.5
Toluidine (meta)	41.89	199.0	0.9887	36.92	..	..	2.4
Cresol (ortho)	42.24	187.0	1.0482	—	..	..	..
Cresol (meta)	42.58	201.0	1.0341	36.82	..	45.17	2.4
Cresol (para)	42.14	200.5	1.0347	36.58	..	..	2.4
Benzyl alcohol	40.20	204.5	1.0463	38.11	..	..	2.4
Ethyl acetate	81.6[1]	77[1]	0.8990[1]	23.87	72.8	30.94	2.6
Propyl formate	78.3[1]	81[1]	0.8982[1]	24.45	63.9	31.37	2.6
Ethyl benzene	64.8[1]	136[1]	0.8759[1]	28.90	8.2	33.88	2.7
Xylene (ortho)	64.4[1]	142[1]	0.8633[1]	28.40	5.8	..	2.6
Xylene (meta)	64.6[1]	139[1]	0.8642[1]	28.48	6.7	34.72	2.6
Xylene (para)	65.7[1]	138[1]	0.8612[1]	28.24	7.5	..	2.6
Isoamyl formate	72.8[1]	123[1]	0.8706[1]	24.58	9.4	34.72	2.4
Methyl isovalerianate	74.6[1]	116[1]	0.8808[1]	24.10	14.15	33.88	2.4
Ethyl butyrate	76.9[1]	120[1]	0.8785[1]	24.44	11.9	34.72	2.5
Isobutyl acetate	78.6[1]	116.5[1]	0.8711[1]	23.62	14.1	33.88	2.5
Ethyl isobutyrate	80.8[1]	110[1]	0.8710[1]	23.26	18.8	..	2.5
Ethyl propionate	78.8[1]	99[1]	0.8907[1]	23.32	28.4	33.05	2.4
Methyl isobutyrate	80.4[1]	92[1]	0.8906[1]	23.72	42.0	32.21	2.5
Methyl butyrate	75.8[1]	102[1]	0.8982[1]	..	24.3	33.05	..
Valerianic acid	69.4	175	0.9301	25.23	..	43.92	2.4
Methyl acetate	78.7	57	0.9286	24.58	..	29.07	2.6
Ethyl acetate	81.6[1]	77[1]	0.8990[1]	23.87	72.8	30.94	2.6
Methyl alcohol	85.7	66	0.7940	22.39	(88.6)[2]	35.14	2.5
Ethyl alcohol	72.75	78	0.8040	22.68	44.0	39.74	2.2
Propyl alcohol (norm)	71.2	97	0.8044	24.23	15.8	41.41	2.3
Butyl alcohol (norm)	69.2	117	0.8094	24.25	(5.0)[2]	44.34	2.3
Butyl alcohol (tert)	79.6	83	0.7887	20.44	31.75	40.37	2.1
Isoamyl alcohol	75.6	131	0.8121	23.56	..	52.94	2.4
Ethyl bromide	89.5	38.0	1.4307	23.23	(387)[2]	27.61	2.8
Ethyl iodide	74.4	72.2	1.9330	28.24	(110)[2]	30.54	3.0
Ethylene chloride	61.5	83.7	1.2569	32.50	62.0	..	3.0
Ethylene bromide	50.5	131.7	2.1823	38.83	9.2	34.30	3.0

Average value of K = 2.53

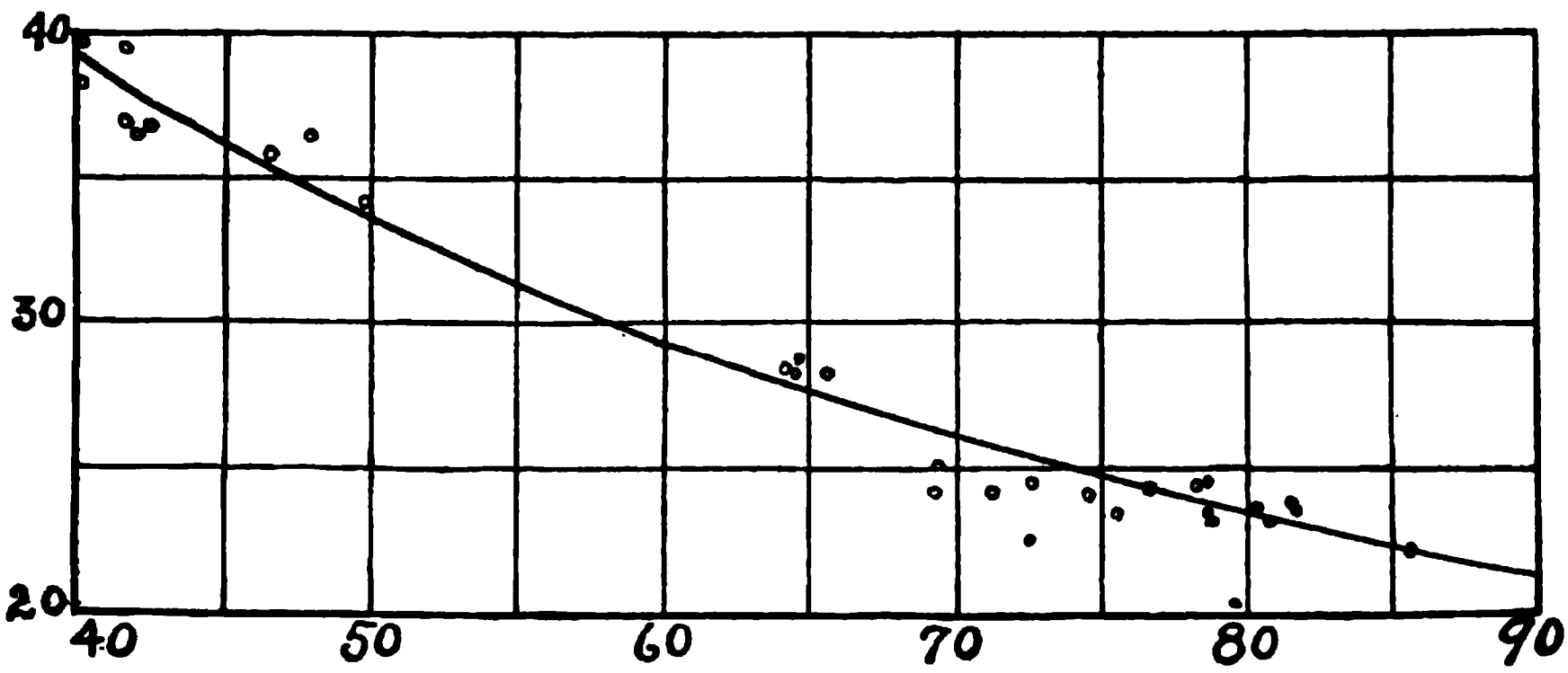
[1] Richards and Stull.

[2] From Landolt and Börnstein.

addition of 0.967 atmosphere, 0.08 milliliter in one liter. This particular value is about double that for water.

Having thus briefly stated the nature of the results, the table containing them may be given at once. In this table, the results are classified according to the composition of the substances, isomeric bodies being placed together. A glance at the table will show that in general the compressibility is large when the surface tension is small, and *vice versa.* Empirically it was found, especially among similar substances, that if the four-thirds power of the surface tension is multiplied by the compressibility, very nearly a constant value is found, especially among similar substances. This approximately constant value is given in the last column.

The results tabulated in the first and fourth columns of figures in this table may well be plotted in a diagram, showing the relation between compressibility and surface tension. As has been said, the general tendency of this curve is expressed by the equation $\beta \gamma^{4/3}$ = constant.



Comparison of the surface tensions and compressibilities of thirty-one compounds of carbon, hydrogen and nitrogen or oxygen. Surface tension (γ) is plotted in the direction of ordinates, compressibility (β) in the direction of abscissae. The curve represents the equation $\beta \gamma^{4/3}$ = constant.

This diagram contains all the results, excepting the four halogen compounds, which have surface tensions too high to correspond with their compressibilities—that is to say, where the value for the constant (3.0) is considerably above the average, 2.5.

That the relationship should be affected by the specific nature of the material need cause no surprise. Indeed it is surprising that the parallelism should be so great as it is. The surface tension may be supposed to be determined chiefly by the cohesive affinity of the substance, or from the molecular point of view, by the attraction between one molecule and another. We have shown that this attraction is probably *one* of the factors entering into the compressibility of a substance, but it is not the

only one. Obviously, not all substances have the same compressibility when subjected to the same increase of pressure, even when they were at first under the same internal tension. Moreover, we must suppose that the compressibility includes within its magnitude not only the change in volume of the outside portions of the molecule, affected by the physical pressure of cohesion, but also the internal alteration of the molecule as well. Hence it is not at all surprising that the specific nature of the substance exercises a distinct effect upon this latter property, and therefore upon the relationship between it and surface tension.

In endeavoring to connect the other properties of material we see in the same way that the specific nature of the substance conceals in part relationships which might otherwise become manifest. For example, the specific gravity would naturally be supposed to be greater in compounds with great surface tension and small compressibility, than in those with small surface tension and great compressibility. The latter substances should be compressed into smaller bulk by the energy of their own cohesive affinity. Such substances also should have high boiling-points and high molecular heats of vaporization. To a certain extent one may trace this connection of properties upon comparing the data for a number of substances taken at random, but it is evident that the matter is not quite so simple as would appear from the above statement. Clearly the specific gravity is enormously affected by the nature of the elements which build up the atom, and variation in the composition may wholly conceal the effect due to surface tension or cohesive affinity. For example, the average specific gravity of hydrogen in an organic compound appears to be only 0.18, because the atomic volume of hydrogen is 5.5, while the specific gravity of carbon in an organic compound is 1.09, and that of oxygen varies between 1.3 and 2.0 on the usually accepted basis. These values are simply obtained by dividing the atomic weight by the usually accepted atomic volume.

On the other hand, in cases of isomeric compounds, regularities appear in the expected direction, except indeed where methyl compounds are concerned. Take for example the substances with the formula $C_6H_{12}O_2$, ethyl butyrate and its isomers. From the figures given in the table it is clear that the order of magnitude in the case of all these properties places ethyl butyrate on one extreme and ethyl isobutyrate on the other extreme with isobutyl acetate in the middle; and that the direction is always that demanded by the reasoning above.

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Summary.—(1) In this paper are given a number of new results on the compressibility, surface tension, boiling point, specific gravity and the vapor pressure at 20° of a number of organic substances.

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(3) This relationship is discussed briefly from the point of view of the theory of compressible atoms.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE BUREAU OF STANDARDS No. 4.]

THE ATOMIC WEIGHT OF CHLORINE.

BY WILLIAM A. NOYES AND H. C. P. WEBER.

Received October 9, 1907.

The ratio of the atomic weights of oxygen and of chlorine is one of extreme importance, on account of the number of atomic weights based either directly or indirectly upon the atomic weight of chlorine.

During the last few years alone, since the determination of the ratio silver to chlorine by Richards and Wells,[1] the atomic weights of a considerable number of the common elements have been determined, basing them on the value of chlorine. These values have been calculated on the oxygen basis, assuming that the ratio silver: oxygen :: 107.93 : 16 is correct. Guye and Ter-Gazarian[2] have called attention to a possible source of error in the chlorate ratio of Stas, correction for which would bring the value of silver down to 107.89. The newly accepted value, 14.01 for nitrogen also points to the lower value of 107.89. Very nearly at the close of this work conclusive evidence has been presented by Richards and Forbes[3] and by Richards and Jones[4] that the value, 107.93 for silver is too high. The only direct comparison between hydrogen and chlorine which we have is that of Dixon and Edgar.[5] In this determina-

[1] This Journal, 27, 459.

[2] Compt. rend., 143, 411.

[3] This Journal, 29, 808.

[4] *Ibid.*, 29, 826.

[5] Phil. Trans., 205, 169. Series A., Chem. News, 91, 263. The determinations by Deutsch (Dissertation, 1905) in the laboratory of Professor Guye, were scarcely of sufficient accuracy to be considered as atomic weight determinations.

tion hydrogen was made to burn in an excess of chlorine. The hydrogen was weighed absorbed in palladium and the chlorine in the liquid form in a glass bulb. The hydrogen and chlorine were caused to unite in a large globe of glass containing a small quantity of water to absorb the hydrochloric acid formed. Corrections were applied for the quantity of chlorine remaining uncombined by titrating the amount of iodine liberated by it from a solution of potassium iodide. A further correction was applied for the amount of chlorine used up in liberating oxygen from water, by determining the amount of oxygen set free.

The fact that there was only one such direct determination of the ratio between chlorine and hydrogen, together with the opportunity afforded of carrying out the determination with hydrogen prepared in the same apparatus used for generating the hydrogen in the recent determination of the ratio of hydrogen to oxygen, made a new determination seem to be worth while.

The method we have used, besides being a direct comparison between hydrogen and chlorine, involves the principle of complete synthesis with the determination of the weights of all the substances reacting and of the reaction products formed. Briefly stated, the method consists in weighing the hydrogen absorbed in palladium, and the chlorine in the form of potassium chlorplatinate. The hydrogen is passed over the heated potassium chlorplatinate from which it removes chlorine to form hydrochloric acid. The hydrochloric acid formed is condensed in a third section of the apparatus and weighed. We have thus the weight of hydrogen used, the weight of chlorine removed, and the weight of hydrochloric acid formed. In this manner two series of ratios, each independent of the other, are obtained.

Working in this manner and with hydrogen prepared under the same conditions and at the same time as that used in the determination of the ratio hydrogen to oxygen by one of us, we believe that we have very favorable conditions for bridging the gap

$$\mathrm{Ag} \rightarrow \mathbf{Cl} \supset \mathbf{H} \rightarrow \mathrm{O}.$$

Purification of Materials and Weighing.

Hydrogen.—The hydrogen used in these experiments was prepared and purified in the same manner as described in a previous paper on the atomic weight of hydrogen.[1] The gas was taken from the generating apparatus at intervals covered by the period of the work on hydrogen. Consequently all remarks concerning its character and purity as used in the hydrogen-oxygen ratio apply to these determinations. As in that work so in this, two methods of generating the hydrogen were employed. In the last series of determinations the hydrogen was obtained by the electrolysis of a solution of barium hydroxide.

[1] Noyes: This Journal, 29, 1720.

Platinum.—The platinum used in the preparation of potassium chlorplatinate was originally obtained in the form of platinum sponge. The preliminary purification consisted in dissolving this in aqua regia and evaporating to remove nitric acid. The separation from other platinum metals was carried on according to the method of Schneider and Seubert as described in Graham Otto's Lehrbuch.[1]

The solution of chlorplatinic acid was boiled for half an hour with excess of caustic soda, acidified and the platinum precipitated as potassium chlorplatinate. The chlorplatinate so obtained was reduced with sodium formate. The platinum black was then heated with dilute hydrochloric acid to remove iron and washed until it commenced to go through as colloidal platinum. It was then redissolved and the process repeatedly gone through until the mother-liquors from the chlorplatinate precipitation were practically colorless and free from other platinum metals. As the same platinum was continually used and underwent a large number of successive solutions and reductions during the preliminary work, it seems safe to assume that it was sufficiently pure.

Potassium Chlorplatinate.—During the preliminary work it was soon discovered that the preparation of chlorplatinic acid by the use of aqua regia was unsatisfactory. The removal of nitric acid by the process of repeated evaporation was tedious and at best uncertain. To overcome this difficulty and eliminate nitric acid entirely, a process of dissolving the platinum electrolytically in purified hydrochloric acid was devised. This proved quite satisfactory and will be described in the following paper. After solution of the platinum in hydrochloric acid had been effected, the solution, which contained approximately 120 grams of platinum and measured 500 cc., was evaporated to about one-half its volume in a glass stoppered wash-bottle. At the same time a current of chlorine was passed through the boiling solution. The chlorine used for this purpose was prepared by the action of pure potassium permanganate upon chemically pure hydrochloric acid which had been previously boiled with a small quantity of permanganate to insure its freedom from bromine compounds. The solution of chlorplatinic acid thus obtained had a beautiful bright color matching almost exactly that of a 0.1 per cent. solution of methyl orange. It contained about 100 grams of hydrochloric acid in excess and after filtration and dilution to one liter was used directly for the precipitation of potassium chlorplatinate. For this purpose a solution of potassium chloride was prepared, using an excess of one-third above the theoretical quantity dissolved in one liter of water. The excess of potassium chloride as well as the excess of hydrochloric acid in the chlorplatinic acid were deemed necessary to check hydrolytic decomposition. For the same reason the precipitation of potassium chlor-

[1] Graham Otto's Lehrbuch, 5th Ed., 4, 1153.

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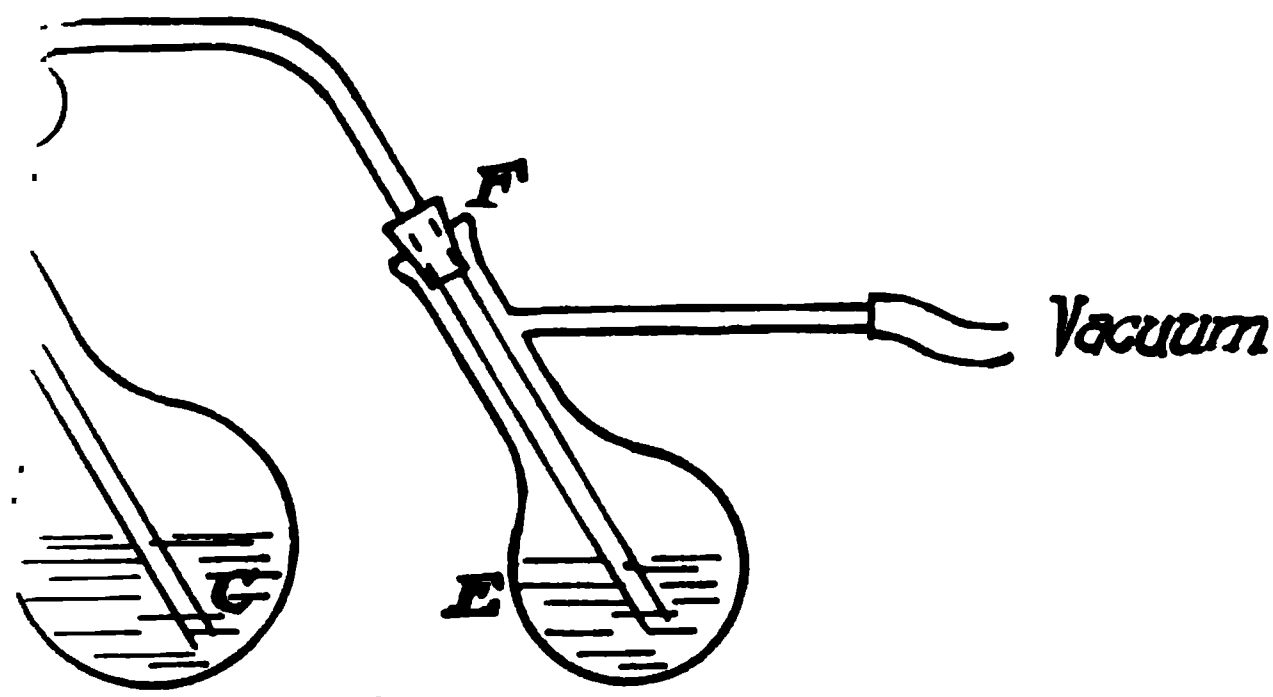

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l). The flasks are then connected by means of the
acuum applied. The capillary tube which is ground
is connected with a carbon dioxide generator, and
been applied, should yield a fairly steady stream of
liquid, so as to insure regular boiling and at the same
y to diminish the vacuum. It is desirable to have a
h as carbon dioxide or nitrogen passing through the
es of reducing substances in the air used, would vitiate
gas passing through the capillary, besides insuring
as a diluent for the steam formed and as such checks

$$H_2O + Br_2 = 2HBr + O.$$

platinate was carried out with as concentrated solutions as practicable. The precipitation itself was carried out by pouring the platinum solution into the potassium chloride in a fine stream, the precipitate meanwhile being agitated thoroughly by a current of air. In some cases as much as four hours were spent in precipitating 300 grams of potassium chlorplatinate. The potassium chlorplatinate so obtained was of a pale yellow color, resembling precipitated sulphur, and was microcrystalline. It was filtered from the mother-liquor by means of a suction pump, washed with water and finally with alcohol and ether. After having been removed from the hardened filter, it was heated for some time in a large platinum dish on an electric air bath until the greater part of the moisture retained had been driven off. The quantity necessary for one determination was then transferred to a hard glass tube. This tube was placed in a cylindrical air bath which could be raised to a temperature of 400°. The potassium chlorplatinate was gradually raised to this temperature, a current of air, dried successively by sulphuric acid and phosphorus pentoxide passing over it continuously. The behavior of the salt under these conditions served as a criterion of its purity. At the exit of the current of gas, a wash-bottle was placed containing a drop of methyl orange. At first a small quantity of moisture and hydrochloric acid passed off. Finally, however, a point was reached where no further hydrochloric acid could be detected in the issuing gas stream. At this point the heating was stopped, usually after the chlorplatinate had been heated to 400° for about seven hours, or more. It seems that the chlorplatinate, when pure, will stand the temperature of 400° indefinitely in a non-reducing atmosphere, without suffering any change chemically. No appreciable quantity of hydrochloric acid could be detected after the hydrochloric acid and water held mechanically had once been driven off. This all, provided the salt was pure to start with. In the first trials, in which the chlorplatinate had been prepared by the use of aqua regia its behavior was entirely different. In these cases decomposition set in in the neighborhood of 250° and seemed to go on progressively throughout the whole mass of the salt.

After having been dried in this manner, the chlorplatinate was transferred to the final apparatus with little or no exposure to the air, through an opening which was sealed off after filling. In this it was subjected to final drying at 350° and evacuation, as described under the manipulations.

Potassium Chloride.—As a starting point for the preparation of pure potassium chloride, the purest commercial article obtainable was taken. This was first recrystallized from a solution made slightly alkaline with potassium hydroxide to remove traces of ammonia which were present. The salt was then redissolved in water and chlorine passed through the

hot solution for several hours, after which it was concentrated and the potassium chloride allowed to crystallize out. Following this the salt was recrystallized five times from water, precipitated three times by alcohol and finally precipitated from aqueous solution by purified hydrochloric acid gas. The crystals in these various processes were separated from the mother-liquors by centrifugal drainage.

This potassium chloride certainly contained less bromine than 1 in 50,000. To test for bromine the following process, a modification of that described by Andrews,[1] was adopted.

Fig. 1.

The flask *A* is fitted with a ground glass joint at *B* which ends in an extremely fine capillary at *C*. The side tube *D* has a trap to prevent spray from being carried over. An ordinary distilling flask is affixed to the end of this side tube with a rubber stopper in such a manner as to bring the side tube well into the bulb of the flask *E*. The flask *A* is charged with 200 cc. of distilled water, 20 cc. of N/5 potassium iodate and 20 cc. of 2 N. nitric acid. The flask *E* contains about 5 cc. of a 4 per cent. solution of potassium iodide (which must not liberate iodine upon being acidified). The flasks are then connected by means of the stopper at *F* and vacuum applied. The capillary tube which is ground into the flask at *B* is connected with a carbon dioxide generator, and after vacuum has been applied, should yield a fairly steady stream of bubbles through the liquid, so as to insure regular boiling and at the same time not appreciably to diminish the vacuum. It is desirable to have a pure neutral gas such as carbon dioxide or nitrogen passing through the capillary, since traces of reducing substances in the air used, would vitiate the results. The gas passing through the capillary, besides insuring regular boiling, acts as a diluent for the steam formed and as such checks the reaction

$$H_2O + Br_2 = 2HBr + O.$$

[1] This Journal, 29, 275.

The flask containing the potassium iodate and nitric acid mixture is then heated on the water bath until 100 cc. have distilled into the flask containing the potassium iodide. If the resulting distillate is colored by the presence of free iodine, the process is repeated after adding water to make up for the quantity distilled off, until a satisfactory blank is obtained. Then 3–5 grams of the potassium chloride to be tested are dissolved in a little water and added to the flask containing the iodate and the volume of the solution made up to 250 cc. again. The distillate containing the free iodine corresponding to the amount of bromine distilled over, is then titrated with a solution of thiosulphate corresponding to 1 mg. of bromine per cubic centimeter. To 5 grams of potassium chloride which had been treated until blank distillates were obtained the following quantities of bromine were added and found:

Added, 1 mg. 0.5, 0.3, 0.1.
Found, 1 mg. 0.52, 0.36, 0.12.

The potassium chloride used for precipitating potassium chlorplatinate contained less than 0.1 mg. bromine in 5 grams or 1 : 50,000. This amount, it is safe to assume, was further reduced in the preparation of potassium chlorplatinate.

Hydrochloric Acid.—The hydrochloric acid used in the preparation of pure hydrochloric acid was free from sulphuric and nitric acid. It was treated by allowing chlorine to bubble through it for one day. Following this, air was bubbled through the acid saturated with chlorine until the chlorine was expelled and the acid was again colorless. Usually the air was left passing through the acid over night, a reduction of about one-fifth in the volume of the acid, due to evaporation, taking place with the removal of the excess of chlorine. During the manipulations in preparing chlorplatinic acid, it was further subjected to the action of chlorine twice, namely, during electrolysis of the platinum and on evaporation of the platinum solution.

Chlorine.—All the chlorine used was generated by the action of pure potassium permanganate on hydrochloric acid which had been previously boiled with a small quantity of potassium permanganate.

Water.—The water used was obtained by redistilling distilled water with alkaline permanganate, rejecting the first part of the distillate until it no longer contained ammonia.

Balance and Weights.—The balance and weights were identical with those described under the atomic weight of hydrogen.[1] The air of the balance case was dried by means of a current of air as described in the previous paper. Each piece of apparatus was weighed with a corresponding counterpoise approaching it within 1 cc. in volume and 30 grams

[1] Noyes, This Journal, 29, 1723.

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Received October 9, 1907.

The ratio of the atomic weights of oxygen and of chlorine is one of extreme importance, on account of the number of atomic weights based either directly or indirectly upon the atomic weight of chlorine.

During the last few years alone, since the determination of the ratio silver to chlorine by Richards and Wells,[1] the atomic weights of a considerable number of the common elements have been determined, basing them on the value of chlorine. These values have been calculated on the oxygen basis, assuming that the ratio silver: oxygen:: 107.93: 16 is correct. Guye and Ter-Gazarian[2] have called attention to a possible source of error in the chlorate ratio of Stas, correction for which would bring the value of silver down to 107.89. The newly accepted value, 14.01 for nitrogen also points to the lower value of 107.89. Very nearly at the close of this work conclusive evidence has been presented by Richards and Forbes[3] and by Richards and Jones[4] that the value, 107.93 for silver is too high. The only direct comparison between hydrogen and chlorine which we have is that of Dixon and Edgar.[5] In this determina-

[1] This Journal, 27, 459.

[2] Compt. rend., 143, 411.

[3] This Journal, 29, 808.

[4] *Ibid.*, 29, 826.

[5] Phil. Trans., 205, 169. Series A., Chem. News, 91, 263. The determinations by Deutsch (Dissertation, 1905) in the laboratory of Professor Guye, were scarcely of sufficient accuracy to be considered as atomic weight determinations.

tion hydrogen was made to burn in an excess of chlorine. The hydrogen was weighed absorbed in palladium and the chlorine in the liquid form in a glass bulb. The hydrogen and chlorine were caused to unite in a large globe of glass containing a small quantity of water to absorb the hydrochloric acid formed. Corrections were applied for the quantity of chlorine remaining uncombined by titrating the amount of iodine liberated by it from a solution of potassium iodide. A further correction was applied for the amount of chlorine used up in liberating oxygen from water, by determining the amount of oxygen set free.

The fact that there was only one such direct determination of the ratio between chlorine and hydrogen, together with the opportunity afforded of carrying out the determination with hydrogen prepared in the same apparatus used for generating the hydrogen in the recent determination of the ratio of hydrogen to oxygen, made a new determination seem to be worth while.

The method we have used, besides being a direct comparison between hydrogen and chlorine, involves the principle of complete synthesis with the determination of the weights of all the substances reacting and of the reaction products formed. Briefly stated, the method consists in weighing the hydrogen absorbed in palladium, and the chlorine in the form of potassium chlorplatinate. The hydrogen is passed over the heated potassium chlorplatinate from which it removes chlorine to form hydrochloric acid. The hydrochloric acid formed is condensed in a third section of the apparatus and weighed. We have thus the weight of hydrogen used, the weight of chlorine removed, and the weight of hydrochloric acid formed. In this manner two series of ratios, each independent of the other, are obtained.

Working in this manner and with hydrogen prepared under the same conditions and at the same time as that used in the determination of the ratio hydrogen to oxygen by one of us, we believe that we have very favorable conditions for bridging the gap

$$\mathrm{Ag} \rightarrow \mathbf{Cl} \supset \mathbf{H} \rightarrow \mathrm{O}.$$

Purification of Materials and Weighing.

Hydrogen.—The hydrogen used in these experiments was prepared and purified in the same manner as described in a previous paper on the atomic weight of hydrogen.[1] The gas was taken from the generating apparatus at intervals covered by the period of the work on hydrogen. Consequently all remarks concerning its character and purity as used in the hydrogen-oxygen ratio apply to these determinations. As in that work so in this, two methods of generating the hydrogen were employed. In the last series of determinations the hydrogen was obtained by the electrolysis of a solution of barium hydroxide.

[1] Noyes: This Journal, 29, 1720.

Platinum.—The platinum used in the preparation of potassium chlorplatinate was originally obtained in the form of platinum sponge. The preliminary purification consisted in dissolving this in aqua regia and evaporating to remove nitric acid. The separation from other platinum metals was carried on according to the method of Schneider and Seubert as described in Graham Otto's Lehrbuch.[1]

The solution of chlorplatinic acid was boiled for half an hour with excess of caustic soda, acidified and the platinum precipitated as potassium chlorplatinate. The chlorplatinate so obtained was reduced with sodium formate. The platinum black was then heated with dilute hydrochloric acid to remove iron and washed until it commenced to go through as colloidal platinum. It was then redissolved and the process repeatedly gone through until the mother-liquors from the chlorplatinate precipitation were practically colorless and free from other platinum metals. As the same platinum was continually used and underwent a large number of successive solutions and reductions during the preliminary work, it seems safe to assume that it was sufficiently pure.

Potassium Chlorplatinate.—During the preliminary work it was soon discovered that the preparation of chlorplatinic acid by the use of aqua regia was unsatisfactory. The removal of nitric acid by the process of repeated evaporation was tedious and at best uncertain. To overcome this difficulty and eliminate nitric acid entirely, a process of dissolving the platinum electrolytically in purified hydrochloric acid was devised. This proved quite satisfactory and will be described in the following paper. After solution of the platinum in hydrochloric acid had been effected, the solution, which contained approximately 120 grams of platinum and measured 500 cc., was evaporated to about one-half its volume in a glass stoppered wash-bottle. At the same time a current of chlorine was passed through the boiling solution. The chlorine used for this purpose was prepared by the action of pure potassium permanganate upon chemically pure hydrochloric acid which had been previously boiled with a small quantity of permanganate to insure its freedom from bromine compounds. The solution of chlorplatinic acid thus obtained had a beautiful bright color matching almost exactly that of a 0.1 per cent. solution of methyl orange. It contained about 100 grams of hydrochloric acid in excess and after filtration and dilution to one liter was used directly for the precipitation of potassium chlorplatinate. For this purpose a solution of potassium chloride was prepared, using an excess of one-third above the theoretical quantity dissolved in one liter of water. The excess of potassium chloride as well as the excess of hydrochloric acid in the chlorplatinic acid were deemed necessary to check hydrolytic decomposition. For the same reason the precipitation of potassium chlor-

[1] Graham Otto's Lehrbuch, 5th Ed., 4, 1153.

was kept fully submerged in liquid air. After the supply of hydrogen had been turned off, the pressure in the apparatus gradually sank until all hydrogen had been used up and all hydrochloric acid condensed. The conditions then were: excess of the chlorplatinate at 350° to 400°; the hydrochloric acid at about —180° and a small fraction of a millimeter residual pressure. The stopcocks of the condensation tube were then closed and the residual gases in the remaining parts of the apparatus pumped out.

The condensation tube was then separated from the remaining parts of the apparatus and the transfer of the hydrochloric acid to the water commenced. The water bulb *L* was plunged into ice water and the condensation bulb *K* removed from direct contact with the liquid air but not entirely beyond the cold vapors. As soon as the pressure of the hydrochloric acid had risen to a small part of an atmosphere, communication was established with the cold water in *L*. After some hydrochloric acid had been absorbed by the water the bulb *L* was cooled by ice and dilute sulphuric acid instead of by ice alone. With the aid of occasional shaking of the absorption bulb the last of the condensed hydrochloric acid was finally absorbed by the water. With cautious manipulation the pressure in the apparatus did not rise above one-half atmosphere during the transfer and remained at a few millimeters at the close. The stopcock *I* between *K* and *L* was then closed, and the apparatus was cleaned, rinsed, wiped and set aside to be weighed. The determinations of the second series required about ten hours from beginning to end. About two hours were consumed in transferring the solidified hydrochloric acid from the condensation to the absorption bulb. The solidified hydrochloric acid resembled snow in appearance and the greater part of it was absorbed by the water without passing into the liquid state. Towards the end of the transfer, when the absorption became less rapid, the remaining hydrochloric acid would liquefy attended by a sudden rise in pressure. Shaking of the absorption tube immediately reduced the pressure and caused the liquid hydrochloric acid to solidify to a glassy solid.

Errors and Corrections.

Hydrogen.—If there were any errors due to a contamination of the hydrogen, they are not apparent. The hydrogen was prepared and purified with all possible precaution. It was repeatedly tested for impurities in the work on hydrogen and oxygen and none or only negligible quantities found.[1]

Two corrections on the weight of hydrogen were found necessary. The first of these was the amount of hydrogen remaining in the chlorplatinate tube at the end of the determination and pumped out with the

[1] Noyes, This Journal, 29, 1724.

residual gases to be analyzed. In eight cases out of the twelve this correction was applied, the maximum being 0.11 mg., the minimum 0.01 mg. and the average 0.047 mg. The determinations affected are 1, 2, 4, 5, 6, 7, 11 and 12. The second correction was due to hydrochloric acid in the palladium tube. Under certain conditions, when the current of hydrogen from the palladium tube was not sufficiently rapid, hydrochloric acid found its way back into the palladium tube, either by diffusion or by being drawn back. Correction for this was readily applied. After having been weighed, the hydrogen apparatus was charged for the succeeding determination. The tube was fitted with a stopcock at both ends, as may be seen in the photograph. After the palladium had been saturated with hydrogen the stopcock farthest from the hydrogen generator was connected to a Liebig flask containing water colored by a drop of methyl orange. The stopcock at *A* was opened while the hydrogen generator was kept going and the hydrogen bubbled through this water before escaping. If the presence of hydrochloric acid made itself known, the palladium was heated to 160° to expel the larger part of the hydrogen it had absorbed and with it any hydrochloric acid present. It was then allowed to cool with a current of hydrogen passing through it and finally filled again at normal temperatures. The hydrochloric acid absorbed by the water was then titrated by N/10 sodium or barium hydroxide. The real weight of the hydrogen was greater than the apparent loss of the tube by the weight of hydrochloric acid found. This correction was applied in determinations 1, 3, 4, 10 and 11 varying between 0.35 and 9.26 mg. and averaging 4.8 mg.

Chlorine from the Loss of the Platinum Tube.—The purity of the chlorine entering into the composition of the chlorplatinate has been spoken of. The maximum amount of bromine in the ingredients used seems to have been 1 in 50,000. The resultant error in the weight would be half of this, since 35.5 grams are replaced by 80, or 1 : 100,000. There seems to be ample justification for considering this point beyond question.

The only other impurities which could possibly affect the results were volatile products in the platinum or elements capable of producing volatile products such as ammonia, water, hydroxyl or oxygen. The method of preparation seems to preclude the possibility of the presence of ammonium salts. The potassium chloride was especially treated to free it from these. Following this there was repeated treatment with chlorine in hot solution. The final heating of the chlorplatinate to 400° over an extended period of time must have caused the destruction and removal of any ammonium compounds which had escaped previous treatment.

The three following impurities, water, hydroxyl or oxygen in the platinum salt, were somewhat more difficult of treatment. It is known that potassium chlorplatinate hydrolyzes in aqueous solution. With this point

in view the precipitation of potassium chlorplatinate was carried out in concentrated solutions with both an excess of potassium chloride and hydrochloric acid, and the mother-liquor was removed as soon as practicable. It was shown that by heating sufficiently long at 400°, all occluded hydrochloric acid could be removed, the chlorplatinate being perfectly neutral after this treatment. This served as indirect evidence that the water was also removed. The agreement between Series 1 and 2 may be considered as additional evidence on this point. In the first series the chlorplatinate had opportunity to become saturated with water vapor at the temperature of 350° during the course of the experiment. In the second series it was in equilibrium with solid hydrochloric acid at —180°. Now hydrochloric acid with its well-known affinity for water vapor may be considered as a very perfect drying agent. Yet the difference between the two series is 1 in 10,000. One hundred and twenty grams of potassium chlorplatinate were used. The presence of 0.05 per cent. moisture in this salt would have raised the atomic weight of chlorine found from 35.184 to 35.244.

Further, in the second series it was noticed that if the condensation tube for the hydrochloric acid was allowed to contain a trace of moisture before the determination was begun this would remain as a trace of aqueous hydrochloric acid after the gas had been transferred from this part of the apparatus to the absorption bulb, the temperature during this transfer remaining, of course, below zero. If, however, the condensation tube was perfectly dry to start with, no such trace of aqueous hydrochloric acid remained, that is, no water had been carried over from the chlorplatinate.

A final test of the chlorplatinate was made for water, hydroxyl or oxygen. One hundred grams of potassium chlorplatinate were treated exactly as for a determination. The chlorplatinate was heated to 400° in a current of dry air, transferred to the apparatus used in the determinations and then evacuated at 350°. Next, pure hydrogen was led over the chlorplatinate until it was completely reduced. The hydrochloric acid formed was led through a narrow U-tube surrounded by a mixture of solid carbon dioxide and alcohol (—78°). Finally, the whole apparatus including the U-tube was evacuated, the final conditions being, 350° in the chlorplatinate tube, —78° in the U-tube and several thousandths millimeters pressure. Upon weighing, the U-tube had shown an increase in weight of 0.9 mg. or 1 in 30,000 on the hydrochloric acid formed.

A number of corrections on the weight of the chlorplatinate tube were necessary. The first of these was necessary on account of the traces of air or nitrogen found in the chlorplatinate tube at the end of the determination. These corrections were found necessary in Experiments 4,

5, 6, and 7, their magnitude being 0.35, 0.76, 0.25 and 2 mg. This air may have been occluded by the chlorplatinate, or it may have come from the water of the absorption tube. It was immaterial how this correction was applied as it lay within the limits of the experimental errors, the maximum correction being 1 : 10,000.

In the second series it sometimes happened that with the most cautious manipulation, chlorplatinate was blown over into the condensation bulb at the beginning of the experiment. After the hydrochloric acid had been absorbed by the water and the apparatus weighed, this chlorplatinate was removed by dissolving in water and weighing first as potassium chlorplatinate and then again as potassium chloride + platinum, after reduction. This correction was applied in Experiments 8, 9 and 11, the amounts being 2.03, 15.0 and 36.5 mg. The apparent loss of the chlorplatinate tube was of course diminished by these quantities.

Hydrochloric Acid.—From the agreement of Series I and II it seems reasonable to assume that no errors were introduced by using water as the absorbing agent for the hydrochloric acid.

The corrections on the apparent gain of the absorption tube were of the following nature: First, the apparent gain was increased by the hydrochloric acid found in the palladium tube and by the hydrochloric acid pumped out from the chlorplatinate tube. The former has been spoken of under hydrogen. In Experiments 1, 6, and 7, there were found 1.27, 0.8 and 0.15 mg. of hydrochloric acid, respectively, in the gases pumped out.

In Experiments 8, 9, and 11, the gain of the absorption tube was diminished by the amount of the chlorplatinate blown over. The corrections were 2.03, 15.0 and 36.5 mg.

The final check on correctness of manipulation, freedom from leaks and other losses was found in the checking of the sum of the weights of the hydrogen and chlorine with the weight of the hydrochloric acid. In the preliminary experiments of both series, discrepancies were found until the details of the determination had been mastered. On this account and on account of other known errors the preliminary determinations were rejected entirely.

Results.

The values obtained are given in the following tables. The weights represent those found after all corrections had been applied. The second part of Experiment 5 was lost.

The value as found for the atomic weight of chlorine is 35.184 with a probable error of ±0.0013. The value obtained for the molecular weight of hydrochloric acid is 36.184 with a probable error of ±0.0012. The combined average of both sections of the two series is 35.184 with a probable error of ±0.0008. This is, of course, on the basis of hydrogen = 1.

	Hydrogen.	Chlorine.	Hydrochloric acid.	At. wt. Cl.	Mol. wt. HCl.
1	0.25394	8.93293	9.18695	35.177	36.178
2	0.28004	9.85590	10.13259	35.195	36.183
3	0.51821	18.23468	18.75359	35.188	36.189
4	0.67631	23.79587	24.47123	35.186	36.185
5	0.58225	20.48158	....	35.177	....
6	0.47989	16.88423	17.36310	35.184	36.182
7	0.64132	22.55816	23.20054	35.175	36.176
			Average of Series I,	35.183 and	36.181
8	0.81608	28.71691	29.53167	35.188	36.187
9	0.83194	29.28055	30.11207	35.195	36.195
10	0.39074	13.74926	14.14078	35.187	36.188
11	0.75560	26.58427	27.33926	35.183	36.182
12	0.77518	27.26746	28.04110	35.177	36.175
			Average of Series II,	35.186 and	36.185
			Total average,	35.184(3)	36.183(7)

On the oxygen basis this value becomes 35.452 if H = 1.00762[1] and 35.461 if H = 1.00787.[2] The values for silver calculated from Richards' ratio and these two values are, respectively, 107.87 and 107.89.[3]

The mean values must be considered as most probable at the present time. These are **35.457** for chlorine and **107.88** for silver.

In eleven experiments 6.41925 grams of hydrogen were united with 225.86017 grams of chlorine and yielded 232.27288 grams of hydrochloric acid. The values obtained from these figures are 35.1846 and 36.1838.

	H + Cl.	HCl.	Difference.
1	9.18687	9.18695	+0.00008
2	10.13594	10.13259	—0.00335
3	18.75289	18.75359	+0.00070
4	24.47218	24.47123	—0.00095
6	17.36412	17.36310	—0.00102
7	23.19948	23.20054	+0.00106
8	29.53299	29.53167	—0.00132
9	30.11249	30.11207	—0.00042
10	14.14000	14.14078	+0.00078
11	27.33982	27.33926	—0.00056
12	28.04264	28.04110	—0.00154
	232.27942	232.27288	—0.00654

[1] Morley's value.

[2] Noyes' recent value.

[3] The value calculated from the results of Dixon and Edgar in the same manner are 35.463 or 35.472 for chlorine and 107.90 or 107.93 for silver. The mean values, 35.467 and 107.91 must be considered, for the present as the most probable which can be calculated from their work. The values for silver are calculated from the results of Richards and Wells, who found that 100 parts of silver gave 132.867 parts of silver chloride, This Journal, **27**, 525.

It may be interesting to note the discrepancies between the weights of hydrogen and chlorine and the hydrochloric acid formed in the individual experiments.

In these eleven experiments there were seven with an apparent loss of weight and four with an apparent gain, the total loss being 1 in 35,000.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE BUREAU OF STANDARDS No. 5.]

PREPARATION OF CHLORPLATINIC ACID BY ELECTROLYSIS OF PLATINUM BLACK.

BY H. C. P. WEBER.

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In the work[1] on the atomic weight of chlorine it was necessary to prepare considerable quantities of chlorplatinic acid free from nitric acid. When using aqua regia to dissolve platinum, considerable difficulty was experienced in removing the last traces of nitric acid by evaporation. When working with as much as 100 grams of platinum, the oft-repeated evaporation to dryness of the solution becomes exceedingly tedious and even at best, yields uncertain results. If the evaporation is carried on with strong hydrochloric acid considerable quantities of material become necessary, while with the use of water there is danger of hydrolytic decomposition of the chlorplatinic acid and consequent contamination of the chlorplatinate with hydroxychlorplatinates.

The process here described overcomes these difficulties and yields a pure solution of chlorplatinic acid. The platinum is prepared for electrolysis by dissolving platinum scraps or platinum sponge in aqua regia. The excess of acid is removed either by neutralization or evaporation, and the platinum solution is reduced by zinc or an alkaline formate, preferably the latter. The solution is decanted from the precipitated platinum, which is then warmed with a little dilute hydrochloric acid to remove iron. The platinum is then transferred to the electrolytic apparatus, the washing of the precipitated platinum being completed in this apparatus, which is constructed as follows:

It consists of a cylindrical tube about 4 cm. in diameter and 35 cm. long, which ends in a narrow glass tube, about 4 mm. bore, which is given the form of a siphon. The anode is a thin disk of sheet platinum which just fits into the tube and is perforated with numerous small pinholes. A small piece of platinum wire is welded to the disk and carried through the glass tube by means of sealing glass. The other end of the platinum wire ends in a glass tube which is carried to the top of the ap-

[1] Noyes and Weber: See preceding article.

paratus and is filled with mercury to make connection for the current. The platinum disk should be about 30 cm. from the top of the apparatus at that point where the tube commences to narrow. After the anode has been sealed into the tube the space below it is filled with glass beads to support the platinum disk, which should rest firmly and evenly upon them. About 5 cm. from the top of the tube three notches are pressed into the glass. From these the cathode chamber is suspended. This consists of a porous porcelain filter about 18 cm. long and 25 mm. in diameter. It is well that the rim of the filter fit snugly in the glass tube so that the filter cap hangs in the tube fairly rigidly.

ANODE

CATHODE

The cathode consists of a sheet of platinum 4 to 5 cm. long and 2 to 3 cm. wide. To it is connected a platinum wire passing through a glass tube. It is suspended from a perforated watch glass, which serves as a cover for the apparatus.

ANODE

The whole apparatus is suspended in a long cylinder by means of a large cork for the purpose of cooling it by running water when necessary. This is not shown in the diagram and may be dispensed with when low currents are used. The apparatus has been used with a current up to 10 amperes. With a current of this strength the cooling jacket is essential, as the apparatus gradually becomes hot.

The platinum is transferred to the tube, being dropped on the anode plate, and is here washed with dilute hydrochloric acid until clean. The wash waters are drawn off by gentle suction at the siphon end *S*. The platinum is then covered with concentrated hydrochloric acid. There should be such a quantity of hydrochloric acid that the liquid stands on

a level with *S* when the porous cylinder is inserted. The porous cylinder is then inserted and filled to the top with hydrochloric acid. After the cathode is inserted the apparatus is ready for electrolysis.

The current may be taken from a 120 volt direct current, lighting circuit with a number of incandescent lamps in parallel with each other and in series with the cell. The cell may be run continuously on 8-10 amperes. The current is used quantitatively in dissolving platinum. During a run of four and a half hours at 8 amperes, 64 grams of platinum were dissolved. The theoretical quantity for 36 ampere hours is 65 grams. While the apparatus is in operation the hydrochloric acid travels from the cathode cell to the anode under the influence both of gravity and electric endosmoses. With the proper adjustments of height of hydrochloric acid in the anode cell, the heavy layer of chlorplatinic acid solution is delivered at the tip of the siphon *S*, drop by drop. If the flow of concentrated solution ceases for any reason it may again be started by gentle suction at *S*. For this purpose it is best to have the siphon tip *S* connected with a receiving flask by means of a double perforated stopper. The acid in the cathode chamber is replenished from time to time as it becomes necessary.

If towards the end of the operation, when the amount of platinum remaining upon the perforated disk becomes small, bubbles of chlorine commence to rise through the liquid, it is an indication that the current density is becoming too great. In this case, bringing fresh acid into the neighborhood of the platinum black and decreasing the current will remedy the chlorine evolution.

In concentrating the solution of chlorplatinic acid after it is so prepared, chlorine is passed through it for a short while. This insures freedom from platinous compounds in case any have been formed during the electrolysis.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 20.]

THE THEORY AND PRACTICE OF THE IODOMETRIC DETERMINATION OF ARSENIOUS ACID.

BY EDWARD W. WASHBURN.

Received November 2, 1907.

1. *Introduction.*—The first application of arsenious acid solution in titrametric analysis was made by Gay Lussac,[1] who used it in chlorimetry with an indigo indicator. Penot[2] later improved the method by the use of strips of starch iodide paper as the indicator and the use of caustic soda as the solvent for the arsenious acid, instead of hydrochloric acid,

[1] Gay Lussac, Ann., 18, 18.

[2] Penot, Dingl. Pol. J., 127, 134 and 129, 286.

which had been used by Gay Lussac. Friedrich Mohr[1] still further improved the process and brought it into its present form by using standard iodine solution instead of chlorine water as the titrating agent and adding the starch indicator directly to the solution. In the earlier editions of his "Titrirmethode" Mohr directs that the arsenious acid solutions be made up with sodium carbonate and that this substance be present in excess during the titration. In the later editions, however, he recommends the substitution of ammonium carbonate as the neutralizing agent, since he finds it to give "a more permanent end-point." Most of the modern text books on analytical chemistry, however, have adopted sodium bicarbonate for this purpose and this is the custom among chemists in this country.

A critical study of this analytical method particularly from the standpoint of the equilibria involved, seems not to have been made, although all of the data necessary for this purpose are now available in the literature of physical chemistry. In fact many of the latest editions of the standard text books on analytical chemistry including Fresenius, Classen, Sutton and Mohr contain incomplete or misleading statements in regard to the theory of the method and the precautions to be observed in applying it. For example to quote from Sutton's "Volumetric Analysis," (1904): "The principle upon which this method of analysis is based is the fact that when arsenious acid is brought in contact with iodine in the presence of water and *free alkali* it is converted into arsenic acid. The alkali must be in sufficient quantity to combine with the hydriodic acid set free, and it is necessary that it should exist in the state of bicarbonate since monocarbonated alkalies *interfere with the color of the blue iodide of starch used as an indicator.*" It might be inferred that the normal carbonate or even the hydroxide would not be objectionable if the use of starch as an indicator were dispensed with.

The development of this method seems to have been purely on empirical grounds and the conditions existing in the solution at the end-point, particularly the conditions necessary for securing a "permanent end-point" are not clearly understood. Owing to this rather unsatisfactory condition of the literature on the subject and in view of the fact that under proper conditions this method is one of the most accurate in the field of analytical chemistry, the following treatment of the subject will be made somewhat detailed. The equilibria involved in the method will first be considered and the calculation of the proper conditions to be observed at the end-point as well as the methods for securing these conditions will be given in detail. The preparation and preservation of standard solutions and the operations and precautions to be observed in applying the method will then be described.

[1] Friedrich Mohr, Lehrbuch der Chemisch-Analytischen Titrirmethode, Ed. 1, 1859.

2. *Theory of the Method.*—When a solution of iodine in potassium iodide is added to a solution containing arsenious acid the reaction which takes place may perhaps best be expressed as follows:

$$H_3AsO_3 + I_3^- + H_2O = H_3AsO_4 + 2H^+ + 3I^- \qquad (1)$$

or in words, arsenious acid reacts with triiodide ion and water to produce arsenic acid, hydrogen ion and iodide ion (the "free iodine" in a 0.1 N iodine solution being practically all in the state of triiodide). This reaction is reversible and can be made to go *completely*[1] in *either* direction according to conditions. The reaction from left to right is made use of in determining arsenious acid, while that from right to left is the basis of a method for determining arsenic acid. We shall consider here only the former case and will proceed to determine the conditions necessary to make the reaction go quantitatively from left to right.

In general an equilibrium can be displaced from left to right by increasing the concentration of the substances on the left-hand side of the equation, or decreasing the concentration of those on the right, or by combining both. In the present instance it is obvious that the concentration of the arsenious acid cannot be increased since the object of the titration is to secure its complete oxidation, and for a similar reason the concentration of the arsenic acid cannot be decreased. The concentration of the I_3-ion must not exceed the first recognizable amount since this determines the end-point. The concentration of the water is, of course, a constant. We are therefore reduced to regulating the hydrogen ion or iodide ion concentration, or both, in order to effect our purpose. Since considerable amounts of iodide are introduced with the free iodine, to keep the latter in solution, and since moreover the presence of iodide ion is necessary to give the proper colored end-point, if starch is used as the indicator,[2] it would be inconvenient to attempt to reduce the iodide ion concentration to a small value. It is obvious, therefore, that the success of the whole titration will depend upon the possibility of maintaining the hydrogen ion concentration at a sufficiently small value.

The most obvious method of reducing the hydrogen ion concentration of a solution is to add an alkali and, since[3] $(H^+)\cdot(OH^-) = K$, by adding sufficient alkali the hydrogen ion concentration can be made as small as desired, the hydroxyl ion concentration, of course, increasing proportionally. In the present case we are, however, limited to a very small value of the hydroxyl ion, since iodine reacts in alkaline solution to form iodide and hypoiodous acid and eventually iodate, as expressed by the following reactions,

[1] By "completely" or "quantitatively" is meant to such a degree that the amount of the substance to be determined, remaining unchanged shall be negligibly small.

[2] See Section 13, Note 6.

[3] Expressions of the form (X) will be used to indicate formula weights of the substance per 1000 cc. of solution.

$$OH^- + I_3^- = HIO + 2I^- \qquad (2)$$

and

$$6OH^- + 3I_3^- = IO_3^- + 8I^- + 3H_2O. \qquad (3)$$

It is thus evident that the hydrogen ion concentration must be kept small enough to allow reaction (1) to proceed quantitatively and yet large enough so that reactions (2) and (3) shall not take place to an appreciable extent. These two conditions might, of course, be mutually contradictory, depending upon the values of the equilibrium constants of the reactions in question.

3. *Calculation of the Upper Limit of Hydrogen Ion Concentration.*—The equilibrium equation for reaction (1) is

$$\frac{(H_3AsO_4)\cdot(H^+)^2\cdot(I^-)^3}{(H_3AsO_3)\cdot(I_3^-)} = K. \qquad (4)$$

The value of this constant is not known very accurately but a value sufficiently exact for the present purpose can be calculated from the data of J. R. Roebuck.[1] From the data in Roebuck's second paper for the experiments made without sulphuric acid (Table 38), the value $K = 3 \cdot 10^{-2}$ for 0° has been calculated. From the experiments made in the presence of sulphuric acid (which greatly complicates the calculation) Luther[2] has recently computed the value $K = 3.3 \cdot 10^{-2}$. For 25° the value would be $K = 7 \cdot 10^{-2}$.

Assuming a desired accuracy of 0.001 per cent. in the titration, which, as will be shown later, it is possible to approach, the calculation of the upper limit of the hydrogen ion concentration is made as follows: 100 cc. of a 0.1 N arsenious acid solution and 100 cc. of a 0.1 N iodine solution are used in the titration, the total volume when the end-point is reached being *250 cc.* The standard iodine solution contains also 0.12 mol. of potassium iodide per liter. The following relations, therefore, exist: 100 cc. of 0.1 N iodine solution give 0.005 mol of triiodide and 0.012 mol. of potassium. 100 cc. of 0.1 N arsenious acid solution give 0.005 mol. of H_3AsO_3. Together they produce 0.01 mol. of iodide to which should be added 0.012 mol., giving 0.022 mol. of iodide present at the end of the titration. There are also produced 0.005 mol. of arsenic acid ($H_3AsO_4 + H_2AsO_4^-$), and 0.01 mol. of hydrogen ion, the latter, however, being neutralized as far as necessary by the presence of some neutralizing agent. These amounts are present in a volume of 250 cc. Assuming the iodide to be 98 per cent. ionized we have

$$(I^-) = 0.022 \cdot 0.98 \cdot 4 = 8.6 \cdot 10^{-2}.$$

Since only 0.001 per cent. of the arsenious acid is to remain at the end of the titration, we have

$$(H_3AsO_3) = 0.00001 \cdot 0.005 \cdot 4 = 2.0 \cdot 10^{-7}.$$

[1] Roebuck, J. Phys. Chem., 6, 395, and 9, 756.

[2] Luther, Z. Elektrochem., 13, 289.

For the concentration of the triiodide we shall assume the amount of free iodine necessary to give the color of the end-point in a volume of 250 cc. As will be explained later,[1] this is found by experiment to be $(I_3^-) = 2.0 \cdot 10^{-7}$.

To obtain the value of (H_3AsO_4) it will be necessary to know the ionization constant for arsenic acid. This can be readily calculated from the conductivity data of Walden[2] in the usual manner and is found to be $4.8 \cdot 10^{-3}$.[3] We have therefore the two equations

$$\frac{(H^+) \cdot (H_2AsO_4^-)}{(H_3AsO_4)} = K = 4.8 \cdot 10^{-3}$$

and

$$(H_2AsO_4^-) + (H_3AsO_4) = 0.005 \cdot 4 = 2.0 \cdot 10^{-2},$$

from which (H_3AsO_4) can be readily obtained in terms of (H^+). Substituting the foregoing values in the equilibrium equation

$$\frac{(H_3AsO_4) \cdot (H^+)^2 \cdot (I^-)^3}{(H_3AsO_3) \cdot (I_3^-)} = 7 \cdot 10^{-2}, \qquad (4)$$

and solving for (H^+) we obtain the result $(H^+) = 1.0 \cdot 10^{-4}$ as the upper limit of the hydrogen ion concentration.[4]

4. *Calculation of the Lower Limit of the Hydrogen Ion Concentration.*—To find the concentration of hydroxyl ion which will produce an error of 0.001 per cent. due to the formation of iodate according to the reaction

$$6OH^- + 3I_3^- = IO_3^- + 8I^- + 3H_2O,$$

it is necessary to know the equilibrium constant for this reaction. This constant can be obtained from the following data:

$$\frac{(H^+)^6 \cdot (IO_3^-)(I^-)^5}{(I_2)^3} = 2.8 \cdot 10^{-47} \text{ (Sammet).}^5 \qquad (5)$$

$$(H^+) \cdot (OH^-) = 1.0 \cdot 10^{-14} \qquad (6)$$

and

$$\frac{(I_2) \cdot (I^-)}{(I_3^-)} = 1.3 \cdot 10^{-3} \text{ (Noyes and Seidensticker).}^6 \qquad (7)$$

Dividing equation (5) by equation (6) raised to the sixth power and then multiplying by equation (7) cubed we get

$$\frac{(IO_3^-) \cdot (I^-)^8}{(OH^-)^6 \cdot (I_3^-)^3} = 6 \cdot 10^{28}, \qquad (8)$$

which is the constant desired. As before, we have total triiodide used

[1] See Section 13, Note 6.

[2] Walden, Z. physik. Chem., 2, 49.

[3] See also Luther, Z. Elektrochem., 13, 297.

[4] It is worth noting that if an accuracy of only 0.1 per cent. is required, this value is still $5 \cdot 10^{-4}$.

[5] Sammet, Z. physik. Chem., 53, 640.

[6] Noyes and Seidensticker, Z. physik. Chem., 27, 357

0.005 mol. Of this 0.001 per cent. = $5.0 \cdot 10^{-8}$ mol. will produce $1/3 \cdot 5.0 \cdot 10^{-8} = 1.67 \cdot 10^{-8}$ mol. of IO_3^-.

We have therefore

$$(IO_3^-) = 4 \cdot 1.67 \cdot 10^{-8} = 6.7 \cdot 10^{-8},$$
$$(I^-) = 8.6 \cdot 10^{-2},$$
$$(I_3^-) = 2 \cdot 10^{-7},$$
$$(OH^-) = x.$$

Substituting in the equilibrium equation (7) above and solving for (OH^-), we find $(OH^-) = 10^{-4}$, a value which, if exceeded, will cause an error of 0.001 per cent. due to the formation of iodate.

The equilibrium constant for reaction (2)

$$OH^- + I_3^- = HIO + 2I^-,$$

is obtained from the following data:

$$\frac{(HIO^-)\cdot(I^-)\cdot(H^+)}{(I_2)} = 10^{-9} \text{ (Sammet)},^1 \tag{8}$$

$$(H^+) \cdot (OH^-) = 1.0 \cdot 10^{-14}, \tag{9}$$

$$\frac{(I_2)\cdot(I^-)}{(I_3^-)} = 1.3 \cdot 10^{-3}. \tag{10}$$

Multiplying (8) by (10) and dividing by (9) gives

$$\frac{(HIO)(I^-)^2}{(I_3^-)\cdot(OH^-)} = 1.3 \cdot 10^2 \tag{11}$$

for the value of this constant. Solving as before for (OH^-) we find $(OH^-) = 10^{-5}$ which is a smaller value than that obtained for reaction (2).

Therefore, since $(H^+) \cdot (OH^-) = 1.0 \cdot 10^{-14}$, we get for the *lower* limit of the hydrogen ion concentration the value $(H^+) = 10^{-9}$. We therefore conclude that if an accuracy of 0.001 per cent. is desired in this titration, the hydrogen ion concentration in the solution when the titration is finished, must lie between the limits, $(H^+) = 10^{-4}$ and $(H^+) = 10^{-9}$. The best value will evidently be the geometrical mean of these two which is $3 \cdot 10^{-7}$. This differs very little from the concentration of hydrogen ion in pure water so that we may state as the final conclusion of the preceding calculations, that, *at the completion of the titration of an arsenious acid solution with standard iodine, the solution should be neutral.*

5. *Solutions of Constant Hydrogen Ion Concentration.*—A solution will automatically keep itself at any desired hydrogen ion concentration even though small quantities of acid or base be added to it, provided it contains something which will remove both hydrogen and hydroxyl ions when acid or alkali are added to the solution. A solution which contains the salt of a weak acid (or base) together with an excess of the acid (or base) has this property of automatically maintaining itself at a practically constant hydrogen ion concentration. If for example acid be

[1] Sammet, *Loc. cit.*

added to a solution containing sufficient amounts of the weak acid HA and its salt MA in the proper proportions, hydrogen ion will be immediately removed by the reaction,

$$H^+ + A^- = HA,$$

and in a similar manner alkali will be neutralized according to the reaction,

$$HA + OH^- = H_2O + A^-.$$

The proper porportions of acid (or base) and salt to use in order to keep the solution at any desired hydrogen ion concentration are readily calculable from the ionization constant of the acid (or base). If the mixture is to be equally efficient in the removal of hydrogen and hydroxyl ions, it is evident that the concentration of the acid (HA), should be equal to that of the ionized salt (A^-), *i. e.*

$$(HA) = (A^-) = \gamma(S) \qquad (a)$$

where γ is the degree of ionization and (S) the total molar concentration of the salt. Combining this relation with the equilibrium equation for the ionization of the acid,

$$\frac{(H^+) \cdot (A-)}{(HA)} = K, \qquad (b)$$

we obtain the result $K = (H^+)$.

That is, *the ionization constant of the acid should be numerically equal to the desired hydrogen ion concentration.* In case no suitable acid can be found which exactly fulfils this condition, one is chosen which most nearly does so. Suppose its constant is

$$K = n(H^+), \qquad (c)$$

then if n is not too large, this acid can be used, provided the ratio of salt (S), to acid (HA), is changed. By combining equations (*a*), (*b*) and (*c*), it is evident that this ratio must have the value,

$$\frac{(S)}{(HA)} = \frac{n}{\gamma}. \qquad (d)$$

In applying these considerations to the problem in hand, since the solution is to be kept neutral, *i. e.*, $(H^+) = (OH^-) = 10^{-7}$, it is evident that the acid chosen should have an ionization constant not far from 10^{-7}. Of the numerous acids which might be used for this purpose we shall consider here only the following acids and their salts.

Acid.	Salt.
NaH_2PO_4	Na_2HPO_4
H_2CO_3	$NaHCO_3$
H_3BO_3	Na_3BO_3

Phosphoric Acid.—The ionization constants of the three hydrogens of this acid are given by the following equations:[1]

[1] The values of these constants have been recently determined in this laboratory by Mr. G. A. Abbott in an investigation which will be published shortly.

$$\frac{(H^+)(H_2PO_4^-)}{(H_3PO_4)} = 1 \cdot 10^{-2}.$$

$$\frac{(H^+)(HPO_4^{--})}{(H_2PO_4^-)} = 2.1 \cdot 10^{-7}.$$

$$\frac{(H^+)(PO_4^{---})}{(HPO_4^{--})} = 5.6 \cdot 10^{-13}.$$

The first hydrogen is a strong acid but the salt of this acid, NaH_2PO_4, acts as a weak acid with the ionization constant 2.10^{-7} and is therefore suitable for the purpose in hand. The ionization constant of the third hydrogen is so small that the ionization of HPO_4^{--} will be entirely negligible. We have, therefore, $(S) = C_{Na_2HPO_4}$, and $(HA) = (H_2PO_4^-) = \gamma_1 C_{NaH_2PO_4}$ where $C_{NaH_2PO_4}$ is the total molar concentration of NaH_2PO_4 and γ_1 its degree of ionization as a salt. Substituting these values in equation (*d*) above we obtain the result

$$\frac{C_{Na_2HPO_4}}{C_{NaH_2PO_4}} = \frac{n\gamma_1}{\gamma}$$

and since γ_1 can be assumed equal to γ, we conclude that the solution at the end of the titration should contain about two mols of Na_2HPO_4 for every mol of NaH_2PO_4 in order to preserve neutrality.

Calculation for Carbonic Acid.—This acid is in general not adapted for the purpose of maintaining a constant hydrogen ion concentration because, being a gas, it escapes gradually from the solution so that its concentration and consequently that of the hydrogen ion is an uncertain quantity. Only when the solution is kept saturated with carbon dioxide at a definite temperature and pressure is the concentration of the carbonic acid in the solution of a definite known quantity. For our present purpose therefore it is necessary to know what concentration of sodium bicarbonate must prevail in a solution *saturated* with carbon dioxide if the concentration of the hydrogen ion is to be 10^{-7}. We have the following ionization equations for the acid.[1]

$$\frac{(H^+) \cdot (HCO_3^-)}{(H_2CO_3)} = 3.04 \cdot 10^{-7}.$$

$$\frac{(H^+) \cdot (CO_3^{--})}{(HCO_3^-)} = 6.04 \cdot 10^{-11}.$$

Here also the dissociation of the second hydrogen in a neutral solution is negligible. In a solution saturated with carbon dioxide at 25° and 1 atmosphere $(H_2CO_3) = 0.0338$. Substituting in equation (*d*) again we obtain

$$\frac{(S)}{0.0338} = \frac{3.04}{\gamma} \text{ which gives } C_{NaHCO_3} = 0.12.$$

Therefore in a 0.12 molar solution of sodium bicarbonate, saturated with

[1] McCoy, Am. Chem. J., 29, 437.

carbon dioxide the hydrogen ion concentration will be about 10^{-7}. The ratio between acid and salt (1:4) is not so favorable as in the case of the phosphate. Owing to the relatively small concentration of the acid, the hydrogen ion concentration will be rather sensitive to the escape of CO_2 from the solution, since to offset this loss, carbonic acid is being continually produced at the expense of the hydrogen ions according to the reaction,

$$H^+ + HCO_3^- = H_2CO_3 = H_2O + CO_2.$$

Boric Acid.—Sammet[1] by the measurement of the E. M. F. of a hydrogen electrode, has determined the hydrogen ion concentration in a solution saturated with respect to both borax and boric acid and found it to be $(H^+) = 6 \cdot 10^{-7}$.

We have therefore three combinations which theoretically should be equally suitable for keeping the solution neutral during the titration.

6. *Test of the Conclusions.*—The conclusions of the foregoing considerations were tested by standardizing an approximately 0.1 normal iodine solution against a 0.1 normal arsenious acid solution. About 100 cc. of the iodine solution were used in each case. The solutions were weighed instead of measured, the end-point being reached by using a very dilute arsenious acid solution, the procedure being that described in the following sections. It will be noticed that the conclusions of the foregoing calculations are completely justified. These results will be discussed later when the procedure has been described.

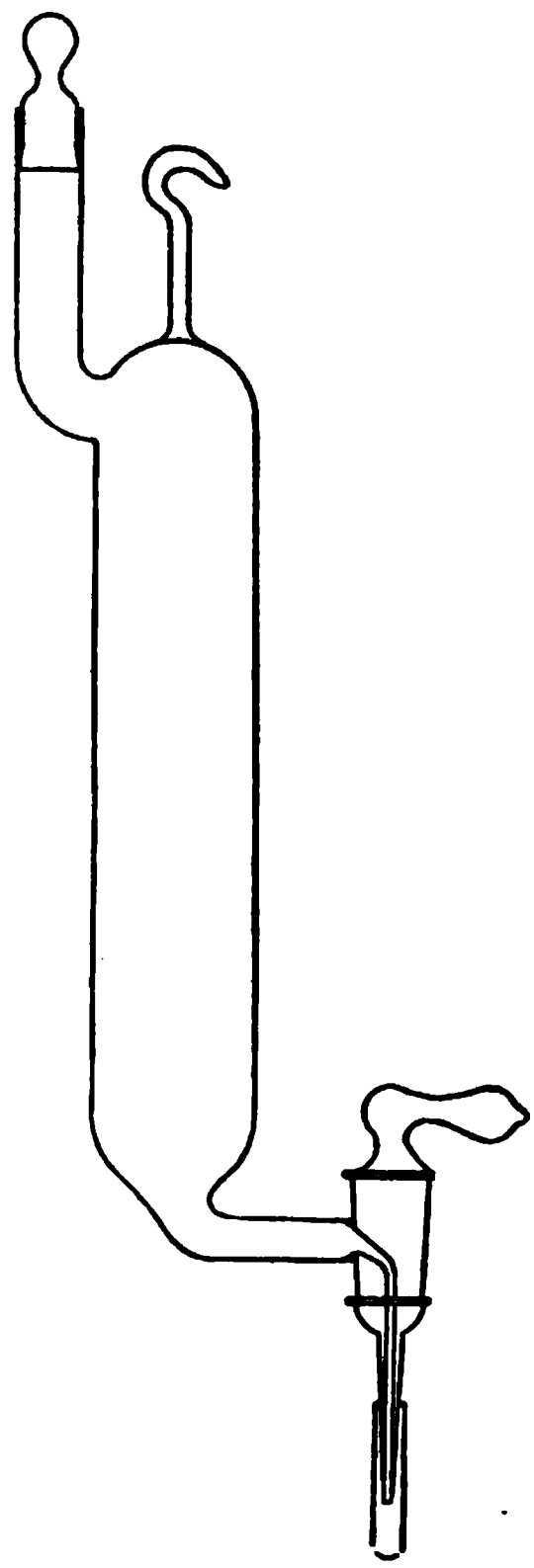
	$NaHCO_3 + H_2CO_3$	$Na_2BO_3 + H_3BO_3$	$Na_2HPO_4 + NaH_2PO_4$	KI alone.
Value of 100 grams of iodine solution in terms of As_2O_3.	0.48737	0.48733	0.48735	—
	0.48736	0.48733	0.48736	—
	0.48738	—	—	—
	0.48736	—	—	—
	0.48735	—	—	—
Blanks in same unit.....	0.000078	0.000078	0.000078	0.000073

Mean, 0.487354.
a. d., 0.000012 = 0.0025 per cent.
A. D., 0.0000040 = 0.00082 per cent.
Max. d., 0.000056 = 0.01 per cent.

7. *Titration by Weight.*—For the most accurate work in titrametric analysis it is necessary to weigh all the solutions used instead of measuring them, and the solutions are conveniently made up on the weight standard system, that is, so that 1000 grams of a normal solution contain one equivalent weight of the substance. Indeed even for work in which only 0.1 per cent. accuracy is required, this method possesses several advantages over the volumetric method and need consume very little

[1] *Loc. cit.*

more time. Its principal advantages are: (1) since graduated vessels are not used, no time need be spent in calibration and no errors are introduced from this source; (2) frequent cleaning of the burettes is not necessary as drops clinging to the sides of the burette do not affect the result; (3) the result is independent of the temperature of the solutions; (4) no time is consumed in allowing the burette to drain, in fact the weight-burette can be weighed in the time usually consumed in drainage.



A convenient form of a weight-burette, devised by Mr. C. A. Kraus, of this laboratory, is shown in the figure. The stopcock and glass cap for the tip are very carefully ground so as to insure a tight joint. The opening for filling the burette is placed at the side so that none of the solution can come in contact with the stopper which is hollow and open at the bottom. In order to permit the entrance of air during the titration, the stopper and the side of the socket are provided with two small holes which can be made to coincide by turning the stopper in its socket. In weighing, the burette is suspended from the balance arm by the hook, a similar burette suspended from the other arm serving as a counterpoise. For most work a suitable weight-burette can also be readily made from a separatory funnel by cutting off the stem, drawing it down to a point, and grinding on a glass cap. Previous to filling the burette, a small quantity of the solution is shaken in it and then allowed to run out. This insures the saturation of the air in the burette by the vapor of the solution.

8. Preparation of Standard Iodine Solutions.—To prepare a liter of approximately 0.1 N iodine solution, 12.7 grams of resublimed iodine are weighed into a small beaker, about 20 grams of pure potassium iodide added, and the whole covered with water and allowed to stand with occasional stirring until solution is complete. The solution is then filtered through an asbestos filter into the stock bottle and sufficient water (best distilled) added to make the volume about 1 liter. The statement is frequently made that iodine solutions cannot be kept very long unchanged and require frequent standardization. In the experience of the author, however, an iodine solution properly prepared and used is one of the most stable of standard solutions. The chief causes of change in titer are losses from evaporation, from particles of dust which may get into the

solution, and from impurities in the water used in preparing the solution. With proper precautions these losses are, however, inappreciable. The neck of the bottle should be kept covered with a beaker to exclude dust, and when the solution is shaken to mix it, care should be taken to avoid wetting the stopper. The solution should always be removed with a pipette, *never by pouring*. It is advisable to allow a newly-prepared solution to stand a few days previous to standardizing and the stock bottle should be kept in a dark place. The following results were obtained for the standardization of an iodine solution at an interval of two months, the solution being in frequent use meanwhile.

November 5th, 1 gram I solution = 0.0048504 gram As_2O_3.
January 8th, 1 gram I solution = 0.0048505 gram As_2O_3.

9. *Preparation of Tenth-Normal Arsenious Acid Solution.*—The arsenious oxide is purified by recrystallization from hot water and by sublimation. After drying in a vacuum over sulphuric acid, about 5 grams of the crystals are placed in a small weighing tube and about 4.95 grams are accurately weighed out into a glass stoppered liter flask which has been previously cleaned, dried and weighed to centigrams. Ten to 12 grams of pure caustic soda are then dissolved in about 30 cc. of water, which has been freshly distilled from an alkaline permanganate solution to insure absence of organic matter and dissolved oxygen. After filtering through asbestos it is added to the flask which is then allowed to stand until solution is complete. The chief impurity which it is necessary to guard against in the caustic soda is *iron*. The grade known as "purified by alcohol" is usually satisfactory for this purpose as it gives a very small blank.

When solution of the arsenious acid is complete (about half an hour), 100 cc. of water are added and a delivery tube is inserted in the flask below the level of the liquid. The delivery tube is connected with a generator supplying carbon dioxide and the gas is allowed to bubble slowly through the solution until saturation is reached. After removing and washing the delivery tube the solution is diluted to nearly a liter with the freshly distilled water. The flask is then placed on the balance pan and water added from a dropper until the weight of the solution is 206.73 times the weight of the As_2O_3 used. After thorough mixing, the solution is ready for use and will preserve its titer almost indefinitely. One thousand grams of the solution correspond to 0.1 equivalent of arsenious acid.

Instead of the above method of preparing the solution with sodium bicarbonate, the following method in which sodium phosphate is used gives fully as satisfactory results and possesses certain advantages as will be pointed out later. In this method the arsenious acid is weighed out as before but is dissolved by adding a strong solution of sodium hydroxide of known strength, the amount added containing 12 grams of NaOH.

When solution of the arsenious acid is complete a solution of pure phosphoric acid containing 0.15 mol of H_3PO_4 is added and the whole made up to the final weight as before.

10. Preparation of the Starch Solution.—This solution, prepared as directed in Treadwell's "Analytical Chemistry,"[1] and preserved in small bottles, is eminently satisfactory. A large supply should be prepared at one time, as solutions prepared at different times are liable to give somewhat different colored end-points. When properly prepared, the first color obtained with iodine should be *pink*. Starch solution which gives a blue or greenish-blue color as the first shade should be rejected. The "soluble starch" of commerce is not to be recommended for the finest work. Two cc. of the starch solution are used in each titration.

11. Standardization of the Iodine Solution against the Arsenious Acid Solution.—About 100 cc. of the arsenious acid solution are removed with a pipette and transferred to a carefully tared Erlenmeyer flask of 500 cc. capacity provided with a rubber (or better, glass) stopper.[2] The weight of the solution to the nearest milligram is then determined, and the flask is placed upon a large sheet of white paper in a good light (preferably north). The weight pipette is then filled with the iodine solution as previously described and is weighed to the nearest milligram. The pipette is placed in its support and the flask containing the arsenious acid solution is held in the hand so that the tip of the pipette touches the inside of the neck of the flask. About 100 cc. of the iodine solution are added and the flask is stoppered lightly and rotated until the yellow color of the iodine disappears. If the arsenious acid solution was prepared with bicarbonate the solution will effervesce, and during the effervescence the flask should be held in a slanting position so that the walls of the flask and not the stopper receive the fine spray thrown up by the effervescence. The titration is continued slowly until finally one drop of the iodine solution produces a permanent yellow color. The flask is then stoppered and allowed to stand while the weight burette is weighed again.

The titration is completed by using a dilute arsenious acid solution. This is prepared by diluting 25 grams of the 0.1 normal solution to a volume of a liter. This 0.0025 N arsenious acid solution is kept in a bottle with a burette permanently attached to it. A titration is finished by adding this dilute solution drop by drop until the yellow color has almost disappeared. Two cc. of the starch solution are then added and the addition of the arsenious acid solution continued until the blue color

[1] Analytical Chemistry, Treadwell-Hall, Vol. 2, p. 513 (1904).

[2] It is convenient to have a number of these flasks ready for use. The lightest flask in the set is used as a partial counterpoise, and the weights of the others are marked on their stoppers. The flasks should be kept in the balance room so as to be under the same conditions of temperature and humidity as the balance.

gives way to a rose color which just matches the color of flask No. 2, of a set of color standards whose preparation will be described below. Before adding the last two or three drops it is best to wait ten or fifteen minutes to insure the completion of the reaction and the attainment of equilibrium. The flask should be protected from the light during this interval. *This end-point when reached (if the flask is kept stoppered and protected from the light) is permanent both in shade and intensity of color for several weeks, and the end-point is sensitive to two drops of the dilute arsenious acid solution, that is, to less than 0.002 per cent.*[1]

12. Preparation of Permanent Color Standards.—A flask containing a solution, the titration of which has just been completed, is made just colorless by the addition of a few drops of the dilute arsenious acid solution. It is then placed under a burette containing a 0.005 N iodine solution and iodine added until a faint permanent yellowish-pink color is produced. In a second flask a solution is made up which exactly matches this color. This is color standard No. 1. It can be made by combining solutions of ferric chloride, copper nitrate and cobaltous nitrate in the proper proportions. Another drop of the dilute iodine solution is then added and a second color standard made up to match this color, which is more of a pink shade. A third drop of iodine solution is then added and the third color standard made to match this color. In titrating a solution the end-point is always taken as the color corresponding to the middle flask in the set of color standards. This shade of pink, which is close to what is known as the "sensitive tint" in polarimetry, is much more sensitive to small changes than are the blue tints obtained by the further addition of iodine.

13. Notes on the Process.—(1) In titrations with the use of sodium bicarbonate as the neutralizing agent it is *absolutely essential* that the solution be kept saturated with carbon dioxide as the calculations indicate; consequently the titration should never be made in a beaker but always in a stoppered flask.[2] This is a precaution which is not mentioned in the text books, but its importance is readily shown by the following experiment. The titration as described above was made in a beaker. When the end-point was reached the solution was stirred for thirty seconds. At the end of this time the solution had become completely colorless. That this was not due to the slowness of the reaction was made evident by

[1] It is best to avoid unnecessary exposure to strong light, especially direct sunlight, since light catalyzes the reaction

$$O_2 + 4H^+ + 4I^- = 2I_2 + 2H_2O$$

which may take place to a slight extent, even in neutral solution, in case dissolved oxygen is present. See Plotnikow, Z. physik. Chem., 58, 214.

[2] The author has found nothing superior to Erlenmeyer flasks for *all* titrametric analyses. They are much more reliable and convenient than the beaker and stirring-rod so frequently used.

adding a few drops of hydrochloric acid to the solution. This caused the evolution of carbon dioxide and the color immediately returned to fade away again on further stirring and consequent escape of carbon dioxide. Unless sufficient free carbon dioxide be present the concentration of hydroxyl ion becomes sufficiently large to cause the formation of an appreciable amount of hypoiodous acid and a consequent fading of the end-point.

Some authors recommend cooling the solution to 0° with cracked ice as giving a more delicate end-point. This is not to be recommended, however, as the reaction is too slow at this temperature. The observed increase in the delicacy of the end-point in the cold solution is simply due to the greater solubility of carbon dioxide at this temperature, so that a solution open to the air does not become alkaline so rapidly as at a higher temperature. *At room temperature and in a closed flask the delicacy and permanency of the end-point are all that could be desired.*

(2) The use of the sodium phosphate has the advantage that the acid is not a gas and its concentration in the solution can be controlled by the operator. Since there is no effervescence when it is used, mechanical loss from this source is impossible. It is to be recommended in preference to the bicarbonate.

(3) The use of the borax-boric acid mixture, while it gives accurate results, is not convenient and has no advantage over the other two. The use of ammonium carbonate as directed by Mohr in his last edition, is still less to be recommended, since owing to the volatility of both the acid and base, the concentration of hydrogen ion is still less under the control of the operator.

(4) In titrating an unknown solution of arsenious acid, the solution, if alkaline, is made neutral with hydrochloric acid; if acid, it is neutralized with sodium hydroxide, using *phenolphthalein* as the indicator. The neutralizing agent, bicarbonate or phosphate, is then added from time to time during the titration and when the titration is nearly completed more of the neutralizing agent is added until the total quantity added amounts to about 5 grams of $NaHCO_3$ or 11 grams of $Na_2HPO_4.12H_2O$ for every 100 cc. of 0.1 N iodine solution required in the titration. The volume at the end of the titration should be about 250 cc. for every 100 cc. of the 0.1 N iodine solution used. Under these conditions the acid produced by the reaction is enough to saturate the solution with carbon dioxide or to produce NaH_2PO_4 in the proper amount to give the molar ratio $\frac{Na_2HPO_4}{NaH_2PO_4} = 2$, at the end-point. The Na_2HPO_4 should be added, in solution, from a burette.

(5) For the determination of small quantities of arsenious acid a 0.01 N iodine solution is used and in this case it is necessary to add the proper

amount of hydrochloric acid to insure saturation with carbon dioxide or to produce the proper amount of NaH_2PO_4, since the acid produced by the reaction is not sufficient. The amount of hydrochloric acid to use in the case of the phosphate has to be obtained by calculation for each case if the highest accuracy is required, so that the use of the bicarbonate is more convenient in this instance. Potassium iodide must also be added to give the proper color for the end-point.

(6) The necessity of the presence of sufficient iodide in the solution to develop the proper color with the starch indicator has been emphasized by Treadwell. If a dilute iodine solution be added to water containing starch, a considerable amount of solution is required before the blue color is produced. The presence of an iodide in the solution causes the color to appear when only a small amount of the iodine has been added. Other salts have a similar effect in developing the color. In order to compare the effect of different salts, the following experiment was made. To a flask containing 250 cc. of water, 3 grams of potassium iodide, and 2 cc. of starch solution, the dilute iodine solution was added until the end-point color was reached. A set of flasks containing 250 cc. of 0.1 molal solutions of the substances named below was then prepared and after the addition of 2 cc. of starch solution, the dilute iodine solution was added to each until the same depth of color was produced as in the first flask. The amounts of iodine solution required in each case is shown in the table.

0.1 molal solution of	cc. of I solution used.
KI	5.5
KCl	17.0
NaCl	17.0
$MgSO_4$	16.0
$Ba(NO_3)_2$	13.0
$(NH_4)_2SO_4$	14.0
(Pure water)	45.0

The color of the end-point in the case of the iodide is of a different shade than the others and is probably due to a different effect. It is usually attributed to the formation of a compound, the statement being made that its presence is essential to the production of the "blue compound" with starch. That this may not be the whole explanation is shown by the effect of the other salts.

14. Determination of Blanks.—In making a blank the solution is made up to correspond exactly to the solution to be titrated but with the omission of the arsenious acid. In addition, it is necessary to add pure potassium iodide (3 grams per 250 cc.) for the reason mentioned in the preceding note. Pure hydrochloric acid is used, if necessary, to insure saturation with CO_2 or to produce the proper amount of NaH_2PO_4. The blanks are made by using an 0.005 N iodine solution whose ratio to the

dilute arsenious acid solution has been determined. With pure materials the blanks, which are purely volume corrections, should be very small, never exceeding a value equivalent to 0.0001 gram As_2O_3. The author has obtained blanks as low as 0.00004 gram As_2O_3, which in an analysis requiring 100 cc. of 0.1 N iodine solution amounts to only 0.008 per cent. The blank is always subtracted in calculating an analysis.

15. *Applications of the Method.*—It is evident from the preceding calculations and experiments that under the proper conditions iodine can be quantitatively reduced to iodide by arsenious acid and that a *definite, permanent and exceedingly delicate end-point* is obtained. The accuracy and definiteness of the end-point makes this method a valuable and convenient one for determining the atomic ratio between arsenious acid and iodine since the materials necessary for the determination can be readily purified and the method is free from any sources of error due to side reactions, adsorption, presence of water, etc., which have to be corrected for in many precipitation methods in atomic weight work. The accurate knowledge of this ratio is important to the analytical chemist since arsenious acid is the most convenient and accurate standard for iodimetry.

BOSTON, November 1, 1907.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE SPECIFIC GRAVITIES OF THE IODIDES OF SODIUM, POTASSIUM, RUBIDIUM, CAESIUM, CALCIUM, STRONTIUM AND BARIUM.

BY GREGORY PAUL BAXTER AND FRANCIS NEWTON BRINK.

Received November 7, 1907.

Attention has been recently called by various authors to large discrepancies and inaccuracies in the present tables of specific gravities.[1] If for no other reason, the interest attached to molecular volume[2] makes the accurate knowledge of specific gravities of considerable importance. Since the specific gravities of the chlorides and bromides of the alkali and alkaline earth metals have already been determined with care,[3] the present research is concerned with the iodides of these elements. Lithium iodide was not investigated because its density has recently been found by one of us.[4]

Among the chief sources of error in specific gravity determinations may be mentioned imperfect drying of the substances and inclusion of mother-liquor by crystals. Both these difficulties were avoided in the

[1] Proc. Am. Acad., 31, 163; Am. Chem. J., 31, 220, 229, 558; Trans. Chem. Soc., 91, 56.

[2] See especially Richards, Proc. Am. Acad., 37, 3, 399; 38, 293; 39, 581.

[3] Landolt-Börnstein-Meyerhoffer.

[4] Baxter, Am. Chem. J., 31, 558.

present research by fusion of the salts, in an atmosphere of nitrogen to prevent decomposition of the iodides.

The purification of the salts from saline impurities and silica is usually of less importance than the elimination of water, since the densities of probable impurities in each case were not far from those of the substances under investigation. Nevertheless, care was taken to remove at least the major part of these impurities.

Of course the usual precautions were taken in setting the pycnometers and in dislodging and boiling out air entangled in the solid material.

The procedure was as follows: The pycnometer employed was devised some years ago for the determination of the specific gravity of very hygroscopic substances,[1] and is a modification of a pycnometer devised by T. W. Richards for the determination of the specific gravity of solids. A weighing bottle was provided with two glass stoppers, one of which was of ordinary shape and was used during the weighing of the substance. Into the other were sealed two capillary tubes which served to fill the bottle with liquid. The weighing bottle and the pycnometer stopper were both made of thick glass in order to avoid distortion when the stopper was inserted. A metallic carriage was used in all the weighings of the bottle.

The salt, contained in a platinum boat, was fused in a current of dry nitrogen in a hard glass tube connected by a ground joint with a bottling apparatus by means of which the boat, after being heated, could be transferred to the weighing bottle without exposure to moist air.[2] Heat was applied gently at first, till the greater portion of the water had been expelled, then the temperature was increased until fusion had taken place and the fused salt was limpid and free from bubbles of gas. The boat was then allowed to cool in a current of nitrogen and, after the nitrogen had been displaced by dry air, the boat was transferred to the weighing bottle and weighed.

The nitrogen was made by passing air through concentrated ammonia and then over hot copper gauze, and was freed from excess of ammonia, as well as from carbon dioxide and moisture, in the usual way by means of dilute sulphuric acid, potassium hydroxide and concentrated sulphuric acid. In the experiments with barium, strontium and calcium iodides the last traces of moisture were removed from the nitrogen by phosphorus pentoxide. Air was purified and dried with the same reagents as in the case of nitrogen.

After the weighing of the salt, the ordinary stopper was removed, enough toluene to cover the boat and salt was quickly poured into the bottle, and the pycnometer stopper, which had been weighed with a small

[1] Baxter and Hines, Am. Chem. J., 31, 220 (1904).

[2] Richards and Parker, Proc. Am. Acad., 32, 59 (1897)

quantity of sirupy phosphoric acid to make the joint tight, was inserted. The pycnometer was placed in a vacuum desiccator, which was then exhausted, and the toluene was allowed to boil gently for some time with frequent jarring to expel the air contained in the crevices of the salt. By means of the capillary tubes the bottle was completely filled with toluene, and, while the pycnometer was immersed as far as possible in a water thermostat at 25°, the toluene was adjusted to a mark etched upon one of the capillaries. The weight of the system was then determined, after the pycnometer had been wiped with a clean, slightly moist cloth and had been allowed to stand in the balance case for a few moments. Prolonged standing in the balance case produced no difference in weight. After a second adjustment of the toluene the system was again weighed. In every case the two weights agreed within a very few tenths of a milligram. The weight of the pycnometer containing the empty boat and filled with toluene was determined six times. From the average of these six weights,[1] the weight of the salt, and the weight of the system including the salt and filled with toluene, was calculated the specific gravity of the salt.

The toluene was dried over metallic sodium and distilled, the first and last portions being discarded. Its specific gravity was determined by means of an Ostwald pycnometer, the capillaries of which were provided with ground glass caps.

Weight of pycnometer. Grams.	Weight of pycnometer filled with water. Grams.	Weight of water. Grams.	Weight of pycnometer filled with toluene. Grams.	Weight of toluene. Grams.
10.6915	19.4087	8.7172	18.2231	7.5316
....	19.4092	8.7177	18.2237	7.5322
10.5911 (without caps)	19.3091	8.7180	18.1237	7.5326
....	....	....	18.1240	7.5329
	Average,	8.7176	Average,	7.5323

Volume of water..... 8.7522 cc.
Weight of toluene in vacuum..... 7.5418 grams
Density of toluene 25°/4°..... 0.8617

The specific gravity of the toluene was also determined with the pycnometer used in the experiments with the salts.

The close agreement of the results for the density of toluene by the two methods shows that the special pycnometer was yielding satisfactory results.

The weights were carefully standardized to tenths of a milligram, and the corrections of the thermometer at 0° and 32.38° were determined. In the foregoing and in the following tables vacuum corrections were ap-

[1] These weights are given below. Since the platinum boat gradually lost in weight, corrections for this loss and for the toluene displaced by the platinum which disappeared, were applied.

plied as follows: toluene, +0.00126; NaI, +0.00019; KI, +0.00024; RbI, +0.00021; CsI, +0.00012; CaI_2, +0.00016; SrI_2, +0.00012; BaI_2, + 0.00009.

Weight of pycnometer and boat. Grams.	Weight of pycnometer and boat, filled with water. Grams.	Weight of pycnometer and boat, filled with toluene. Grams.
22.5227	33.3865	31.9073
....	33.3865	31.9066
....	....	31.9068
....	....	31.9066
....	....	31.9069
....	....	31.9070
	Average, 33.3865	Average, 31.9069

Weight of water	10.8638 grams
Volume of water	10.9072 cc.
Weight of toluene in vacuum	9.3960 grams
Density of toluene 25°/4°	0.8615
Average density of toluene by the two methods	0.8616

By evaporating toluene which had been in contact with the fused salts it was shown that all the salts examined are insoluble in toluene.

All the substances were prepared by acting on the carbonates or hydroxides of the metals with pure hydriodic acid and crystallizing the iodides, in most cases twice. This hydriodic acid was made from iodine which had been once distilled from aqueous potassium iodide and once reduced to hydriodic acid with hydrogen sulphide and set free by distilling the hydriodic acid with pure potassium permanganate, with intermediate boiling of the hydriodic acid for some time to remove cyanogen.[1] The final product was thus twice distilled from an iodide, the iodide in the second case being already of considerable purity. Hence chlorine and bromine must have been eliminated.[2] The iodine was then once distilled from pure water, and again reduced with hydrogen sulphide. The resulting hydriodic acid was filtered to remove sulphur and finally distilled shortly before use, with a quartz condenser. After distillation the acid was always colored brown with free iodine, and the iodides made from it, even after crystallization, showed traces of free iodine. During the fusion of the salts, however, this iodine must have been expelled and any iodates must have been decomposed. The hydriodic acid was free from sulphate.

The salts were all mixed with pure ammonium iodide before fusion, in order to prevent the production of basicity. In the case of the alkalies a very small quantity of ammonium iodide was sufficient to produce the desired effect, but in the case of the alkaline earths even a considerable amount did not completely prevent basicity.

[1] Richards and Singer, Am. Chem. J., 27, 205.

[2] Baxter, Proc. Am. Acad., 40, 421 (1904).

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Sodium Iodide.—Commercial sodium carbonate was three times crystallized from aqueous solution in a platinum dish. The carbonate was next dissolved in a slight excess of hydriodic acid and the solution of sodium iodide was evaporated to crystallization in a glass dish. The crystals were freed from mother-liquor by whirling in a platinum centrifugal machine.[1] In many cases the fused material, when dissolved in water and tested with phenolphthalein, gave a slight alkaline reaction. In no case, however, did this alkalinity, which was determined by titration against hundredth-normal acid, correspond to more than five hundredths of a milligram of sodium oxide, hence no measurable effect could have been exerted upon the result.

Weight of salt in vacuum. Grams.	Weight of displaced toluene in vacuum. Grams.	Density of NaI. 25°/4°.
2.9209	0.6879	3.658
1.4635	0.3436	3.670
3.1410	0.7376	3.669
2.5324	0.5953	3.665
4.8574	1.1425	3.663
	Average,	3.665[2]

Potassium Iodide.—Acid potassium carbonate was recrystallized, once in glass and twice in platinum. The final product was then essentially free from sodium. The pure bicarbonate was converted into iodide, as in the case of sodium. The fused material when dissolved in water was neutral to phenolphthalein in every case.

Weight of salt in vacuum. Grams.	Weight of displaced toluene in vacuum. Gram.	Density of KI. 25°/4°.
3.2078	0.8859	3.120
3.4772	0.9660	3.101
3.2367	0.8948	3.117
2.0803	0.5740	3.123
3.2059	0.8861	3.117
3.1652	0.8759	3.114
3.5595	0.9862	3.110
	Average,	3.115[3]

[1] Richards, This Journal, 27, 110 (1905). Baxter and Coffin, *Ibid.*, 28, 1582 (1906).

[2] Previous determinations of the density of this salt are as follows:

Filhol, Ann. chim. phys. [3], 21, 415 (1847) 3.450
Favre and Valson, Compt. rend., 77, 579 (1873) ..... 18°, 3.654

[3] Previous determinations of the density of this salt are as follows:

Boullay, Ann. chim. phys. [2], 43, 266 (1830) ..... 3.078 and 3.104
Karsten, Schw. J., 65, 394 (1832) 2.908
Playfair and Joule, Man. Chem. Soc. 2, 401 (1845) ..... 13°, 3.048 and 3.070
Filhol, Ann. chim. phys. [3], 21, 415 (1847) 3.056
Schiff, Ann., 108, 21 (1858) 2.850

Rubidium Iodide.—Rubidium material was purified by five crystallizations as dichloriodide from dilute hydrochloric acid solution. The dichloriodide was dried and converted to chloride by heating to 150°. The chloride was changed to sulphate with sulphuric acid, the sulphate to hydroxide with barium hydroxide, and the excess of barium hydroxide was removed by carbon dioxide. The rubidium hydroxide was neutralized with an excess of hydriodic acid and the iodide crystallized. The fused salt, when dissolved in water, was in every case neutral to phenolphthalein.

Weight of salt in vacuum. Grams.	Weight of displaced toluene in vacuum. Gram.	Density of RbI. 25°/4°.
3.0856	0.7741	3.434
3.4762	0.8719	3.435
3.4942	0.8735	3.447
3.2558	0.8156	3.439
3.3482	0.8398	3.435
	Average,	3.438[1]

Caesium Iodide.—Caesium iodide was made from caesium dichloriodide which had been five times recrystallized.[2] The dichloriodide was converted to iodide exactly as in the case of rubidium. The fused salt when dissolved in water was in both experiments neutral to phenolphthalein.

Weight of salt in vacuum. Grams.	Weight of displaced toluene in vacuum. Gram.	Density of CsI. 25°/4°.
4.0805	0.7795	4.510
4.2525	0.8124	4.510
	Average,	4.510[3]

Calcium Iodide.—Marble was dissolved in nitric acid and the solution

Buignet, Jahresb., 14, 15 ..... 2.970
Schröder, Ann., 192, 298 (1878) ..... 3.077, 3.081, and 3.083
Spring, Ber., 16, 2724 (1883):
fused ..... 20°, 3.012
fused, subjected to 20,000 atmospheres pressure ..... 22°, 3.110
fused, twice subjected to pressure ..... 20°, 3.112
Buchanan, Am. J. Sci. [4], 21, 25 (1906), by displacement of mother-liquor ..... 24.3°, 3.043

[1] Previous determinations of the density of this salt are as follows:
Clarke, Am. J. Sci. [3], 13, 293 (1877) 3.023
Setterberg, Oefvers. Stockh. Akad. Förh., 6, 23 (1882) 3.567
Buchanan, Am. J. Sci. [4], 21, 25 (1906), by displacement of mother-liquor ..... 24.3°, 3.428

[2] Wells, Am. J. Sci. [3], 43, 17 (1892).

[3] Previous determinations of the density of this salt are as follows:
Setterberg, Oefvers. Stockh. Akad. Förh., 6, 23 (1882) 4.537
Béketoff, Landolt-Börnstein-Meyerhoffer 4.523
Buchanan, Am. J. Sci. [4], 21, 25 (1906), by displacement of mother-liquor ..... 22.8°, 4.508

was heated with an excess of lime. The filtered solution was acidified and evaporated to crystallization and the product was three times recrystallized.[1] Calcium carbonate was precipitated from the nitrate by means of ammonium carbonate and was thoroughly washed by decantation. The carbonate was then dissolved in hydriodic acid and the iodide crystallized. The salt when fused alone in a current of nitrogen, after solution in water is strongly basic. This basicity was partially remedied by mixing the calcium iodide before fusion with a considerable quantity of ammonium iodide, and keeping the temperature below the sublimation point of ammonium iodide until practically all the water was expelled. The salt was then heated to fusion long enough to eliminate all of the ammonium iodide. The alkalinity of each sample is indicated in terms of calcium oxide in the third column of the table. The density of calcium oxide as given in Landolt-Börnstein-Meyerhoffer is 3.3; hence, the following determinations could not have been appreciably affected by this impurity.

Weight of salt in vacuum. Grams.	Weight of displaced toluene in vacuum. Gram.	Percent. of CaO	Density of CaI_2. 25°/4°.
2.1287	0.4636	0.09	3.956
2.1919	0.4777	0.23	3.953
2.5370	0.5523	0.05	3.958
		Average,	3.956[2]

Strontium Iodide.—A solution of strontium chloride was heated first with hydrogen sulphide and then, after filtration, with strontium hydroxide and sulphate.[3] From the filtered solution the strontium was precipitated as carbonate with ammonium carbonate, the carbonate was washed and reprecipitated as carbonate. The product, after being washed, was dissolved in hydriodic acid and the iodide was crystallized.

Weight of salt in vacuum. Grams.	Weight of displaced toluene in vacuum. Gram.	Per cent. of SrO.	Density of SrI_2. 25°/4°.
1.9305	0.3657	0.10	4.549
2.2813	0.4323	0.03	4.547
1.8901	0.3573	0.30	4.558
2.2628	0.4284	?	4.551
2.1664	0.4105	0.00	4.547
2.7070	0.5135	0.01	4.542
2.6167	0.4199	0.16	4.549
		Average.	4.549[4]

[1] Richards, This Journal, 24, 374 (1902).

[2] Only one previous determination of the density of this salt exists:

Ruff and Plato, Ber., 35, 3612 (1902)..... 20°, 4.9

[3] Richards, Proc. Am. Acad., 30, 375 (1894).

[4] Bödeker found the value 4.415 at 10°. Die Beziehung zwischen Dichte und Zusammensetzung bei festen und liquiden Stoffen. Leipzig, 1860.

In spite of the addition of ammonium iodide to the salt before fusion, the fused salt was slightly basic in all but one experiment. Since the density of strontium oxide is 4.6,[1] the basicity could not have affected the results.

Barium Iodide.—Barium nitrate was five times crystallized and converted into carbonate by precipitation with ammonium carbonate. From the carbonate the iodide was formed as in the case of calcium and strontium. Here also ammonium iodide failed to prevent basicity completely, but as in the cases of strontium and calcium, the error is too small to consider, since the density of barium oxide is about 5.3.[1]

Weight of salt in vacuum. Grams.	Weight of displaced toluene in vacuum. Gram.	Percent. of BaO.	Density of BaI_2. $25°/4°$.
4.8746	0.8110	0.10	5.179
3.9124	0.6551	0.18	5.146
5.0750	0.8525	0.21	5.129
4.3577	0.7292	0.07	5.149
3.9504	0.6615	0.14	5.146
4.3432	0.7270	0.12	5.147
5.0332	0.8414	0.07	5.154
		Average,	5.150[2]

It is to be noted that the values obtained by earlier experimenters are in most cases lower than ours, owing probably to the dangers mentioned at the beginning of this paper.

As a result of this investigation the densities of the following salts at 25° referred to water at 4° were found to be:

Sodium iodide	3.665
Potassium iodide	3.115
Rubidium iodide	3.438
Caesium iodide	4.510
Calcium iodide	3.956
Strontium iodide	4.549
Barium iodide	5.150

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ON THE OXIDATION OF HYDRAZINE. II.

BY A. W. BROWNE AND F. F. SHETTERLY.

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Curtius and Schulz[3] have shown that alcoholic solutions of hydrazine hydrate and iodine react quantitatively in accordance with the equation

$$5N_2H_4.H_2O + 4I = 4N_2H_4.HI + 5H_2O + N_2,$$

[1] Landolt-Börnstein-Meyerhoffer.

[2] Filhol obtained the value 4.917. Ann. chim. phys. [3], 21, 415 (1847).

[3] J. pr. Chem. [2], 42, 521–49 (1890).

and that this reaction may be used as the basis of a method for determining the strength of solutions of hydrazine hydrate.

Rimini[1] found that the reaction between hydrazine sulphate and potassium iodate could be expressed by the equation

$$5N_2H_4.H_2SO_4 + 4KIO_3 = 5N_2 + 12H_2O + 2K_2SO_4 + 3H_2SO_4 + 4I.$$

For the determination of hydrazine he recommended the following procedure: A weighed sample of the material to be examined is treated with a measured excess of potassium iodate. After the solution has been heated (in order to expel the liberated iodine) and then cooled, it is acidified with dilute sulphuric acid, and the excess of potassium iodate is determined in the usual way with a standard solution of sodium thiosulphate. Rimini stated that bromates react with hydrazine, when heated, but that chlorates do not react at all.

Riegler[2] devised a method for the determination of formaldehyde, which consists in the measurement of the volume of nitrogen liberated from a known amount of hydrazine sulphate (in presence of the formaldehyde) by the action of a solution of iodic acid. From the difference between the volume of nitrogen formed under these conditions, and the volume liberated from the same amount of hydrazine sulphate (in absence of formaldehyde), may be calculated the amount of formaldehyde present. In a subsequent article[3] Riegler suggested the use of a gasometric method of alkalimetry, based upon the reaction between hydrazine sulphate and sodium iodate. Still later[4] he recommended for the determination of iodides. a method consisting in the measurement of the nitrogen liberated by the addition of an excess of hydrazine sulphate to the iodate solution obtained by oxidizing the iodide in alkaline solution with potassium permanganate.

Stollé[5] described an iodometric method for the determination of hydrazine. The titration is carried out in the presence of primary potassium or sodium carbonate. Rupp[6] maintained that the presence of sodium potassium tartrate or sodium acetate leads to more satisfactory results, but that the necessary delay of 15 minutes in awaiting the end of the reaction detracts from the practical value of the iodometric method.

Schlötter[7] found that the reduction of the alkali bromates with hydrazine sulphate proceeds quantitatively, and made use of this fact in his gas

[1] Gazz. chim. ital., 29, I, 265–69 (1899); Atti. accad. Lincei Roma [5], 15, II, 320; Chem. Zentr., 1906, II, 1662.

[2] Z. anal. Chem., 40, 92–4 (1901).

[3] *Ibid.*, 41, 413–19 (1902).

[4] *Ibid.*, 46, 315–18 (1907).

[5] J pr. Chem. [2], 66, 332–38 (1902).

[6] *Ibid.* [2], 67, 140–42 (1903).

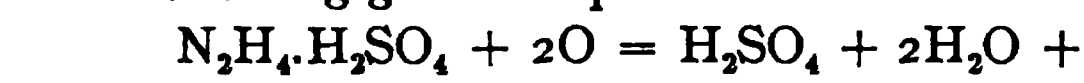
[7] Z. anorg. Chem., 37, 164–71 (1903).

volumetric method for the determination of bromates.[1] He also ascertained that iodic acid may be reduced quantitatively to hydriodic acid, by the action of hydrazine sulphate, but that potassium chlorate undergoes quantitative reduction only after prolonged boiling.[2]

Roberto and Roncali[3] expressed the reaction between chlorine water and hydrazine sulphate by means of the equation

$$N_2H_4.H_2SO_4 + 2Cl_2 = N_2 + 4HCl + H_2SO_4.$$

They recommended the use of hydrazine sulphate in the analysis of chloride of lime and of Javelle solution. In a later article[4] they have described the action of oxidizing agents upon hydrazine sulphate with the aid of the following general equation:



$$N_2H_4.H_2SO_4 + 2O = H_2SO_4 + 2H_2O + N_2.$$

After expressing the reaction between potassium permanganate and hydrazine sulphate in acid solution by means of an erroneous equation,[5] they predicted the probable usefulness of hydrazine sulphate in the analysis of oxidizing agents in general, including peroxides and chlorates.

Jannasch and Jahn[6] found that in alkaline solutions potassium iodate and potassium bromate are easily reduced by hydrazine sulphate, but that potassium chlorate is decomposed only to a limited extent. When potassium chlorate is treated with hydrazine sulphate in the presence of hydrogen peroxide and nitric acid, considerable quantities of hydronitric acid are formed. This result was tacitly attributed by Jannasch and Jahn to the action of nitric acid[7] upon the hydrazine sulphate, in accordance with the observations of Sabanejeff and Dengin.[8]

The present article contains the description of a series of experiments illustrating the respective action of potassium chlorate, potassium bromate, potassium iodate, chlorine, bromine, and iodine upon hydrazine sulphate in acid solution. These experiments have been performed primarily for the purpose of investigating the possible formation of hydronitric acid as one product of the above reactions, and of determining the yield of the acid under certain specified conditions.

[1] Z. anorg. Chem., 37, 172–76 (1903).

[2] *Ibid.*, 38, 184–90 (1904).

[3] L'Industria chimica, 6, 93–5 (1904); Chem. Zentr., 1904, I, 1294.

[4] L'Industria chimica, 6, 178–79 (1904); Chem. Zentr., 1904, II, 616.

[5] Compare Petersen, Z. anorg. Chem., 5, 1–7 (1893); also Medri, Gazz. chim. ital., 36, I, 373 (1906); Chem. Zentr., 1906, II, 459.

[6] Ber., 38, 1576–89 (1905).

[7] In the light of certain experiments performed in this laboratory (Browne, This Journal, 27, 551–55 (1905); see also the results shown in Table I of the present article) it is apparent that the formation of hydronitric acid under the conditions prevailing in the experiments of Jannasch and Jahn might also be attributed to the action of either one or both of the other oxidizing agents present: hydrogen peroxide and potassium chlorate.

[8] Z. anorg. Chem , 20, 21–29 (1899).

Preparation of Solutions.—The solution of hydrazine sulphate contained 10.000 grams of the salt per liter. The solutions of potassium chlorate, bromate, and iodate contained 9.4226, 12.8418 and 16.4575 grams of the respective salts per liter. All four solutions were therefore almost exactly equimolecular.

General Procedure Followed in the Experiments.—A measured volume of the hydrazine sulphate solution was placed in a one liter round bottom flask provided with a four-hole rubber stopper through which passed (1) the stem of a separatory funnel, (2) a thermometer, (3) a glass tube serving as the air inlet, and reaching to the bottom of the flask, and (4) a glass elbow tube communicating with the condenser. After the desired amount of concentrated sulphuric acid had been added, the solution was heated to about 80°, and a measured amount of the oxidizing agent was added drop by drop through the separatory funnel. Throughout the entire experiment a current of air was in general drawn through the apparatus, in order to carry the hydronitric acid from the flask through the condenser into the absorption apparatus (which contained 5 cc. of a 10 per cent. solution of silver nitrate, 2 cc. of a 10 per cent. solution of sodium acetate and 35 cc. of distilled water), for a description of which reference may be made to the first article of the present series.[1] After the entire quantity of the oxidizing agent had been added, the solution was boiled until all of the hydronitric acid had been distilled from the flask. In the quantitative experiments the amount of hydronitric acid formed was determined as usual by the method of Dennis and Isham.[2] In certain experiments the yields of ammonia were determined by making the residual solution (after the hydronitric acid had been completely expelled) alkaline with sodium hydroxide and distilling with usual precautions into standard hydrochloric acid. The yields of both hydronitric acid and ammonia have been calculated on the basis of the equation[3]

$$2N_2H_4 + 2O = HN_3 + NH_3 + 2H_2O.$$

Results Obtained in the Experiments.—The results are tabulated under five different heads: (1) action of potassium chlorate upon hydrazine sulphate; (2) action of potassium bromate upon hydrazine sulphate; (3) action of potassium iodate upon hydrazine sulphate; (4) action of chlorine, bromine and iodine, respectively, upon hydrazine sulphate;

[1] Browne and Shetterly, This Journal, 29, 1305–12 (1907).

[2] *Ibid.*, 29, 18 (1907).

[3] This equation recalls the work of E. Fischer (Ber., 10, 1336 (1877)), who obtained diazobenzenimide and aniline (analogous to hydronitric acid and ammonia) by the action of iodine upon phenylhydrazine. This analogy in the behavior of the organic and the inorganic derivatives of hydrazine, as well as the interesting question of the possible formation of certain new inorganic compounds of hydrogen and nitrogen as intermediate products of the oxidation of hydrazine, is now under investigation in this laboratory, and will be discussed in detail in a future communication.

(5) action of potassium chlorate, bromate and iodate, respectively, upon hydrazine sulphate in presence of silver sulphate.

(1) *Action of Potassium Chlorate upon Hydrazine Sulphate.*—When heated together in presence of free sulphuric acid, aqueous solutions of these substances react with the formation of considerable quantities of hydronitric acid and ammonia. The acid was identified by the series of qualitative tests described in an earlier article.[1] The details of a number of experiments are given in Table I.

TABLE I.

Number of experiment.	$N_2H_4.H_2SO_4$ solution. cc.	$KClO_3$ solution. cc.	Concentrated H_2SO_4 cc.	AgCl obtained. Gram.	Yield HN_3. Per cent.	Portion of distillate containing bulk of HN_3.
1	100	28.6	10.0	0.0738	13.39	..
2	100	28.6	10.0	0.0840	15.24	..
3	100	33.3	10.0	0.0814	14.77	..
4	100	33.3	10.0	0.0874	15.86	..
5	100	50.0	0.5	0.0204	3.70	6
6	100	50.0	5.0	0.1207	21.90	5
7	100	50.0	10.0	0.0822	14.91	4 and 5
8	100	50.0	25.0	0.0942	17.09	1 and 2
9	100	50.0	50.0	....	....	1
10	100	55.6	0.5	0.0299	5.42	6
11	100	55.6	5.0	0.0426	7.73	5
12	100	55.6	10.0	0.0947	17.18	4 and 5
13	100	55.6	25.0	0.0513	9.30	1 and 2
14	100	55.6	50.0	....	....	1
15	100	66.7	10.0	0.1091	19.79	..
16	100	66.7	10.0	0.1237	22.44	..

From these experiments it is apparent that the yield of hydronitric acid does not vary in any regular way with the concentration of the oxidizing agent or of the sulphuric acid. In fact, the magnitude of the yield seems to depend fully as much upon the method adopted in bringing the two substances together, in heating the mixture, and in distilling off the hydronitric acid, as upon any other factor. The liberation of chlorine during the experiment militates against the production of a large yield of the acid. That the presence of a considerable amount of sulphuric acid is necessary seems to be shown by the low yields obtained in Experiments 5 and 10. A separate series of experiments (each performed in duplicate), the results of which are given in column 7 of Table I, has shown, moreover, that the formation of hydronitric acid takes place most readily within a certain range of concentration of sulphuric acid. In each of these experiments the distillate was divided into six 25 cc. fractions. To each fraction was added 1 cc. of a 9 per cent. ferric chloride solution. From the depth of color shown by the various fractions the relative amounts of hydronitric acid present were then roughly estimated.

[1] Browne, This Journal, 27, 551–55 (1905).

In every case the bulk of the acid was found in one or at most two of the fractions; moreover, as the concentration of sulphuric acid was increased, the formation of the hydronitric acid took place earlier in the experiment. Thus in Experiments 5 and 10, in which but 0.5 cc. of sulphuric acid was present, the hydronitric acid came over in the sixth fraction, while in Experiments 9 and 14, in which 50 cc. of sulphuric acid were present, the hydronitric acid appeared in the first fraction. These facts cannot be explained on the ground that hydronitric acid might be expected to distil over more rapidly from solutions strongly acidified than from solutions but slightly acidified with sulphuric acid. Curtius and Rissom[1] have shown that when an aqueous solution of hydronitric acid is distilled, almost the entire amount of the acid passes over with the first fourth of the liquid. It is consequently legitimate to infer from the presence of the greater part of the hydronitric acid in the sixth fraction obtained in Experiments 5 and 10, for example, that the formation of the acid does not readily take place until toward the close of the experiment, when the concentration of the sulphuric acid has become sufficiently high.

For the purpose of determining the yield of ammonia formed under conditions substantially similar to those under which the largest yield of hydronitric acid had been obtained, four additional experiments were performed. Care was of course taken to use sufficient potassium chlorate to insure the complete oxidation of the hydrazine, since any hydrazine remaining unoxidized would have been at least in part distilled over with the ammonia when the residual solution was heated after having been made alkaline. In each of the experiments, 100 cc. of the hydrazine sulphate solution and 10 cc. of concentrated sulphuric acid were employed. In the first two, 66.7 cc. of the potassium chlorate solution were used in each case; in the last two, 77.8 cc. The yield of ammonia in the four experiments amounted respectively to 48.76, 40.99, 31.64 and 30.06 per cent.

(2) *Action of Potassium Bromate upon Hydrazine Sulphate.*—Aqueous solutions of these substances react when heated together in presence of free sulphuric acid, forming appreciable quantities of hydronitric acid and ammonia. The results obtained in a series of experiments (parallel in the main with the experiments in which potassium chlorate was used) are shown in Table II.

The best yields of hydronitric acid were obtained when 5 cc. of sulphuric acid were taken. The decrease in yield observed as the concentration of sulphuric acid was increased beyond this limit is at least partially attributable to the greater difficulty of preventing, in strongly acid solution, the liberation of free bromine during the course of the reaction.

[1] J. pr. Chem. [2], **58**, 261–309 (1898).

TABLE II.

Number of experiment.	$N_2H_4.H_2SO_4$ solution. cc.	$KBrO_3$ solution. cc.	Concentrated H_2SO_4. cc.	AgCl obtained. Gram.	Yield HN_3 Per cent.
1	100	28.6	5.0	0.0298	5.41
2	100	28.6	10.0	.....	....
3	100	33.3	5.0	0.0368	6.68
4	100	33.3	10.0	0.0217	3.94
5	100	50.0	0.0	0.0058	1.05
6	100	50.0	0.5	0.0104	1.88
7	100	50.0	5.0	0.0341	6.18
8	100	50.0	10.0	0.0252	4.57
9	100	55.6	0.5	0.0179	3.25
10	100	55.6	5.0	0.0346	6.28
11	100	55.6	10.0	0.0095	1.72
12	100	55.6	25.0	0.0017	0.31

The yield of ammonia was determined in four additional experiments, in each of which 100 cc. of hydrazine sulphate solution were taken. The other details were respectively as follows: potassium bromate solution, 66.7, 66.7, 77.8, 77.8 cc.; concentrated sulphuric acid, 5, 10, 5, 10 cc.; yield of ammonia, 9.77, 3.91, 1.21, 1.21 per cent.

(3) *Action of Potassium Iodate upon Hydrazine Sulphate.*—Preliminary experiments seemed to indicate that no hydronitric acid was formed by the interaction of these substances. In the four experiments subsequently performed, distilled water was consequently substituted for the usual absorbing solution (containing silver nitrate and sodium acetate), in order to facilitate the detection of minute amounts of hydronitric acid. In each of the experiments 100 cc. of hydrazine sulphate solution were employed. The amounts of the other substances were respectively as follows: potassium iodate solution, 28.5, 33.3, 50, 50 cc.; concentrated sulphuric acid, 5, 5, 5, 10 cc. Some difficulty was experienced in keeping the iodine that was liberated during the reaction from passing over into the distillate, especially in the fourth experiment, in which 10 cc. of sulphuric acid were employed. In certain cases it was found necessary to shake a portion of the distillate (to be tested for hydronitric acid) with metallic mercury before adding the ferric chloride solution, in order to remove the small quantities of free iodine that were unavoidably distilled over. In no case was the slightest indication of the presence of hydronitric acid observed.

In the fifth experiment 200 cc. of the hydrazine sulphate solution, to which had been added 20 cc. of sulphuric acid, were treated with 133.3 cc. of the potassium iodate solution. The solution was heated until the evolution of gas had ceased, and was then made alkaline with sodium hydroxide. No indication of the presence of ammonia was observed when a moistened piece of red litmus paper was suspended above the liquid in the flask. The subsequent addition of 2 mg. of solid ammonium

chloride (corresponding to 0.5 per cent. yield of ammonia) to the same solution caused the litmus paper to turn distinctly blue.

(4) *Action of Chlorine, Bromine, and Iodine, Respectively, upon Hydrazine Sulphate.*—In the foregoing experiments it was observed (as might have been expected) that the tendency for the free halogen to appear during the course of the reaction varied directly with the atomic weight of the halogen. In the experiments with potassium chlorate, for example, it was comparatively easy to keep the free chlorine from passing over into the absorption apparatus, while in the experiments with potassium iodate it was found necessary to employ some caution in the addition of the oxidizing agent, and in the regulation of the temperature at which the reaction was permitted to take place, in order to prevent the carrying over of considerable quantities of free iodine. In almost every case it was found possible, however, by the exercise of proper precautions, to effect the reduction of the free halogen by the hydrazine sulphate still remaining in the solution. From these facts it is obvious that the hydrazine sulphate is in each case virtually subject to the action of two different oxidizing agents during the course of the experiment, either one or both of which might be responsible for the production of the hydronitric acid.

In order to investigate qualitatively the behavior of the free halogens toward hydrazine sulphate, with reference to the formation of hydronitric acid, a series of experiments was performed in which hydrazine sulphate was treated in both acid and alkaline solution with chlorine, bromine and iodine solutions, respectively. The chlorine solution was prepared (immediately before the experiments were performed) by saturating distilled water at room temperature with chlorine gas. The bromine solution contained about 6.9 grams of bromine per liter. The iodine solution contained about 11.0 grams of iodine, and 22 grams of potassium iodide per liter. The details of the experiments are given in Table III.

TABLE III.

Number of experiment.	$N_2H_4.H_2SO_4$ solution. cc.	Oxidizing solution. cc.	Conc. H_2SO_4. cc.	NaOH. Grams.	Result of tests for HN_3.
1	50	100 (chlorine)	5	.	Small amount of HN_3
2	50	100 "	5	.	" " " "
3	50	100 "	.	5	" " " "
4	50	100 "	.	5	" " " "
5	50	100 (bromine)	5	.	No HN_3
6	50	100 "	5	.	" "
7	50	100 "	.	5	Trace of HN_3
8	50	100 "	.	6	" "
9	50	100 (iodine)	5	.	No HN_3
10	50	100 "	5	.	" "
11	50	100 "	.	5	" "
12	50	100 "	.	5	" "

For the experiments in which sulphuric acid was used the general procedure was briefly as follows: the oxidizing solution was first added slowly to the acidified hydrazine sulphate solution, with frequent shaking in order to hasten the reaction. When the reduction of the halogen was complete (in the experiments with iodine it was found necessary to heat the solution at intervals), the solution was distilled, and the first fractions were carefully tested for hydronitric acid. For the experiments in which sodium hydroxide was used, the general procedure was as follows: The oxidizing solution was first brought into contact with the sodium hydroxide (in the form of a 20 per cent. solution). The hydrazine sulphate was then added, and the solution was shaken until the evolution of gas had nearly ceased. After having been heated for a short time, the solution was slightly acidified with sulphuric acid and was distilled. Careful tests for hydronitric acid were made, as before, upon the first fractions of the distillate. In no case were indications given of the formation of any very considerable quantity of hydronitric acid. When chlorine was used it was found that a small amount of hydronitric acid was formed in both acid and alkaline solution. With bromine, traces of the acid were formed in alkaline solution, but none in acid solution. With iodine there was no formation of hydronitric acid in either acid or alkaline solution. From these results the conclusion may be drawn that the tendency of the free halogens to form hydronitric acid as one of the oxidation products of hydrazine sulphate is but slight in any case, and that this tendency varies inversely with the atomic weight of the halogen.

It seems reasonable also to infer that the liberation of the halogens in the chlorate, bromate and iodate experiments must be unfavorable to the production of large yields of hydronitric acid, even though precautions are taken to keep the free halogen in any case from passing over into the absorption apparatus. Since the liberation of a given amount of iodine would presumably militate more strongly against the production of hydronitric acid than would the liberation of a corresponding amount of bromine or of chlorine, and since the liberation of iodine takes place more extensively than that of the other halogens, it is by no means surprising that hydronitric acid was not formed in the experiments with potassium iodate. It has moreover been shown by experiment that even potassium chlorate, under conditions otherwise very favorable to the formation of hydronitric acid, does not produce appreciable yields of the acid in presence of potassium iodide. Two experiments were performed in which the procedure adopted in Experiments 6 and 16, Table I, was carefully duplicated. In these cases, however, 0.64 gram and 0.85 gram of potassium iodide were dissolved in the acidified hydrazine sulphate solution before the (gradual) addition of the potassium chlorate solution. In both cases the tests for hydronitric acid gave negative results.

(5) *Action of Potassium Chlorate, Bromate and Iodate, Respectively, upon Hydrazine Sulphate in Presence of Silver Sulphate.*—A natural supposition to be made on the basis of the facts discussed in the preceding paragraphs is that if the liberation of halogen in the chlorate, bromate, and iodate experiments could be entirely prevented, the yield of hydronitric acid might be appreciably increased. In the experiments recorded in Table IV this condition has been realized by the addition in each case, of 1 gram of silver sulphate, in solid form, to the acidified solution of hydrazine sulphate, prior to the introduction of the oxidizing solution. The procedure was in all other particulars the same as in the earlier experiments with these oxidizing agents.

TABLE IV.

Number of experiment.	$N_2H_4.H_2SO_4$ solution. cc.	Oxidizing solution. cc.	Concentrated H_2SO_4. cc.	AgCl obtained. Gram.	Yield HN_3. Per cent.	Yield NH_3. Per cent.
1	100	($KClO_3$) 78.0	10	0.0734	13.32	15.64
2	100	" 78.0	10	0.0707	12.83	16.96
3	100	($KBrO_3$) 66.7	10	0.0374	6.79	25.25
4	100	" 66.7	10	0.0642	11.65	27.42
5	100	(KIO_3) 66.7	10	0.0520	9.43	12.68
6	100	" 66.7	10	0.0615	11.16	16.16

These experiments show clearly that while in the case of the chlorate solution the presence of silver sulphate does not increase the yield of hydronitric acid, with the bromate solution a slight increase, and with the iodate solution a very marked increase is to be noted. In other words, the influence of the silver sulphate in augmenting the tendency of the chlorate, bromate, and iodate solutions to form hydronitric acid from hydrazine sulphate in acid solution, varies directly with the atomic weight of the halogen.

Summary.

When potassium chlorate or bromate is brought into contact with hydrazine sulphate in the presence of sulphuric acid, the hydrazine is not completely oxidized to nitrogen and water. A secondary reaction takes place which may be expressed by the equation

$$2N_2H_4 + 2O = HN_3 + NH_3 + H_2O.$$

With potassium chlorate the highest yields obtained were 22.44 per cent. HN_3, 48.76 per cent. NH_3; with potassium bromate, 6.68 per cent. HN_3, 9.77 per cent. NH_3. With potassium iodate under similar conditions no formation of HN_3 or of NH_3 was observed. The amount of hydronitric acid formed, consequently, decreases with increase of the atomic weight of the halogen.

By the action of the free halogens upon hydrazine sulphate but little hydronitric acid was obtained in any case. When chlorine was used, a small amount of the acid was formed in both acid and alkaline solution.

With bromine, traces were formed in alkaline solution, but none in acid solution. With iodine there was no formation of hydronitric acid in either acid or alkaline solution. The slight tendency of the free halogens to produce hydronitric acid from hydrazine sulphate, consequently decreases with increase of the atomic weight of the halogen.

The maximum yields of hydronitric acid and ammonia obtained in a series of experiments with potassium chlorate, bromate, and iodate, in the presence of sulphuric acid and silver sulphate, were as follows: with potassium chlorate, 13.32 per cent. HN_3, 16.96 per cent. NH_3; with potassium bromate, 11.65 per cent. HN_3, 27.42 per cent. NH_3; with potassium iodate, 11.16 per cent. HN_3, 16.16 per cent. NH_3. The influence of the silver sulphate in augmenting the yield of hydronitric acid consequently varies directly with the atomic weight of the halogen.

The behavior of a number of other oxidizing agents toward hydrazine sulphate is now under investigation in this laboratory.

CORNELL UNIVERSITY,
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ON THE REACTION BETWEEN LIME AND SULPHUR.

BY R. W. THATCHER.

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The compounds which may be formed by the union of calcium and sulphur, either with or without oxygen, are quite numerous and varied in their properties. They have been extensively studied in connection with the theoretical principles involved in the replacement of oxygen by its analogous element sulphur. Recently, the subject has been given a very important economic bearing by the very extensive use of solutions prepared by boiling together in water, lime, sulphur, and sometimes other ingredients, and applied as insecticides for scab on animals and for soft-bodied scale insects on fruit trees. Some idea of the extent to which this wash is being used on the Pacific Coast States may be obtained from the fact that a single firm has recently installed in California a plant which is producing at each single boiling fourteen carloads of a concentrated lime-sulphur solution of twelve times the strength in which it is used in orchard practice, while at least two other firms are manufacturing similar concentrated solutions on a large scale, and a very much larger amount of the wash is produced by home-boiling in orchards and sheep camps.

The formulae which have been used for the preparation of the insecticide wash have differed widely. The various modifications of the original formula have been based on a great variety of conceptions as to the nature of the compounds formed in the wash and their insecticidal properties, none of which, however, were based on any accurate knowl-

edge of the reactions involved. Because of this, we began in the laboratory, in 1902, a study of the nature of the reactions involved and the compounds formed when lime, sulphur, and other ingredients, are boiled together in water. This study has been continued, as opportunity has permitted, up to the present time. We have now sufficient data from which to draw certain conclusions, which are presented herewith. Reports of the progress of these investigations have been issued as Bulletins Nos. 56 and 76 of this Station, and complete details of our analytical data up to the date of their issuance may be found therein. The earlier investigations showed clearly that, whereas it had been supposed that the wash was a very complex mixture containing many different compounds, in reality it contains only two characteristic compounds, calcium pentasulphide and calcium thiosulphate, small amounts of sulphite or sulphate being occasionally found as a result of oxidation subsequent to the formation of the true products of the reaction.[1] Later, studies were carried on with a view of ascertaining whether the proportion of these two ingredients, or of lime and sulphur in the solution can be varied by changing the conditions of boiling.

The results of the analyses of a few typical solutions, made according to formulae representing the extremes of those which have been suggested for the preparation of the wash, are included in Table I. Many others, of varying formulae and conditions of boiling, have been prepared and analyzed, but the general relationships found were the same as in those here recorded, and the analytical data are omitted in order to economize

TABLE I.

COMPOSITION OF LIME-SULPHUR SOLUTIONS PREPARED ACCORDING TO DIFFERENT FORMULAS.

Formula.				Sulphur in 100 cc. of solution.						
Lime. Parts.	Sulphur. Parts.	Salt. Parts.	Water. Parts.	Total. Grams.	As pentasulphide. Grams.	As thiosulphate. Gram.	As sulphite and sulphate. Gram.	Lime in 100 cc. of solution. Grams.	Ratio lime to sulphur in solution.	Ratio pentasulphide to thiosulphate sulphur.
2	1	1	25	3.94	3.19	0.72	0.03	2.06	1:1.91	1:4.43
1	1	1	25	3.94	3.18	0.73	0.03	2.03	1:1.94	1:4.36
1	1	..	25	3.94	3.19	0.72	0.03	2.01	1:1.96	1:4.43
1	1⅔	..	25	3.97	3.25	0.69	0.03	2.04	1:1.96	1:4.53
1	2½	..	25	3.95	3.16	0.71	0.05	1.32	1:2.24	1:4.43

space. Our results show that when freshly slaked lime and sulphur, either with or without the addition of salt, are boiled together in an excess of water, in open vessels, they dissolve in the average proportions of 1 part calcium oxide to 1.94 parts sulphur, if the lime is in excess, and of 1 part calcium oxide to 2.24 parts sulphur if the latter is present in excess. The solubility of lime, as calcium hydroxide, in water in the

[1] Haywood has independently arrived at similar conclusions, see This Journal, 28, 245, and Bureau of Chem. Bull. No. 101, 10.

proportions used, is sufficient to account for nearly two-thirds of the difference between these ratios, and its solubility in the lime-sulphur mixture may be somewhat greater. It is very probable, therefore, that the proportion of calcium in combination with sulphur in the solution is the same regardless of which of the two components is used in excess, the increased amount of lime in solution when the latter is in excess being simply dissolved calcium hydroxide. This excess of calcium hydroxide may after a time unite with some of the calcium pentasulphide of the solution, since if solutions prepared with an excess of lime are allowed to stand for several days, or longer, they frequently deposit bright red or yellow crystals of oxysulphides of calcium. These latter are probably of variable composition, since they have been variously stated to be

$$3CaO.CaS_4.12H_2O,\ 2CaO.CaS_3.10 \text{ or } 11H_2O,\ 5CaO.CaS_5.20H_2O.$$
$$4CaO.CaS_4.18H_2O, \text{ or } 3CaO.CaS_3.14 \text{ or } 15H_2O.^1$$

The comparatively slight variations in the proportions of the ingredients found in the several solutions are easily accounted for, either by analytical errors due to the fact that the methods used have been very recently devised and may not be quite perfect,[2] or by some chemical changes produced by too prolonged boiling of the solutions, resulting in subsequent rearrangements according to reactions which have been pointed out by Haywood.[3]

The possible reactions between calcium hydroxide and sulphur are represented by the following equations:

(1) $3Ca(OH)_2 + 12S = CaS_2O_3 + 2CaS_5 + 3H_2O$ or $CaO:S::1:2.286$

(2) $3Ca(OH)_2 + 8S = CaS_2O_3 + 2CaS_3 + 3H_2O$ or $CaO:S::1:1.524$

(3) $3CaOH_2 + 4S = CaS_2O_3 + 2CaS + 3H_2O$ or $CaO:S::1:0.762$

and perhaps intermediate ones, resulting in the formation of CaS_4 or CaS_7. Schöne[4] states that when calcium sulphide and sulphur are boiled together in water, they invariably dissolve in the proportions to form CaS_4 and CaS_5. Since our analyses have shown, however, that after allowing for the lime in solution as calcium hydroxide the ratio of lime to sulphur in combination is always about 1 : 2.24, it appears that equation (1) above represents the reaction by which the chemical union takes place when these two substances are boiled together in water in open vessels. Our results show, furthermore, that any excess of either lime or sulphur above these proportions is left uncombined in the mixture, and has no more insecticidal value than it would have if boiled with water alone. Hence the most economical use of these ingredients for the preparation of lime-sulphur compounds for insecticide purposes re-

[1] See Watts' Dictionary, Vol. 1, 667.

[2] The methods used were practically identical with those described by Haywood; This Journal, 28, 247–248, and Bureau of Chem. Bull. No. 101, 9.

[3] This Journal, 28, 249.

[4] Pogg. Ann., 117, 58.

quires that they be taken in the proportions on 1 part lime to 2.24 parts sulphur. Since in practice, lime is rarely absolutely pure, a somewhat larger proportion of it, say 1 part to 2 parts sulphur, had best be used. Further, it is sometimes desirable to have an excess of undissolved lime in the mixture, as "whitewash" in order to make it more easily visible when sprayed on the tree. In such cases, the lime must be used in larger proportions than 1 part to 1.94 parts sulphur or none will remain undissolved.

It will be noticed in the above table of analyses that the ratio of sulphur in sulphide form to that in thiosulphate form is always slightly less than would be produced by the reaction represented by equation (1), *i. e.*, 1 to 5. This is undoubtedly due to secondary oxidation of pentasulphide to thiosulphate during the boiling in open vessels, according to the reaction suggested by Haywood,[1] since both Haywood's experience and our own have demonstrated that the longer the mixture is boiled after the sulphur is dissolved, the greater the proportion of thiosulphate sulphur becomes. Since the chief, if not the only, insecticidal value of the mixture lies in the pentasulphide sulphur which it contains, care should always be observed in preparing solutions for use as insecticides to prevent this oxidation as far as possible. This can be done by shortening the boiling and by covering the cooking vats so as to exclude the air as much as possible.

Concentrated Lime-Sulphur Solutions.—Within the past two years several firms have been experimenting with the view of producing highly concentrated solutions of lime-sulphur compounds to be shipped and sold for insecticide use. A considerable number of these have been submitted to us for analysis. Some of the results of these analyses are presented in Table II. In each of the three different brands represented, or solutions manufactured by three different firms (represented by A, B, and C respectively), the samples which were first produced are recorded first, and the following analyses show the results of later attempts to increase the concentration and proportion of sulphur in solution. These solutions are made by boiling by means of steam heat, a thick "milk of lime" with the proper amount of very finely divided sulphur, in tanks from which the air is excluded as completely as possible by means of heavy wooden covers. The boiling is continued until the maximum amount of sulphur which will stay in solution after cooling is dissolved. The manufacturers state that further concentration of the solutions beyond the point represented by the final sample of each brand results in the separation of crystals on cooling. All these samples have now been standing in our laboratory for six months or more, and show

[1] This Journal, 28, 249.

no deposition of crystals; hence, they probably represent approximately saturated solutions.

TABLE II.

COMPOSITION OF CONCENTRATED LIME-SULPHUR SOLUTIONS.

Sample No.	Sulphur in 100 cc. of solution. Total. Grams.	As pentasulphide. Grams.	As thiosulphate. Grams.	As sulphite and sulphate. Gram.	Lime in 100 cc. of solution. Grams.	Ratio lime to sulphur in solution.	Ratio pentasulphide to thiosulphate sulphur.
A_1	20.30	17.68	2.05	0.57	8.17	1:2.48	1: 8.62
A_2	32.38	29.79	2.02	0.57	12.49	1:2.72	1:14.75
A_3	35.63	34.18	1.23	0.22	13.74	1:2.49	1:27.78
B_1	23.64	19.00	4.10	0.54	10.50	1:2.29	1: 4.63
B_2	25.47	22.58	2.08	0.81	10.66	1:2.39	1:10.85
B_3	30.21	27.80	1.74	0.67	11.54	1:2.61	1:15.92
B_4	35.89	34.29	1.48	0.12	14.28	1:2.52	1:23.18
C_1	17.65	14.00	3.32	0.33	8.67	1:2.04	1: 4.19
C_2	26.98	24.82	1.88	0.28	10.47	1:2.58	1:13.20
C_3	34.07	32.03	1.80	0.24	13.30	1:2.56	1:17.78

It will at once be noticed from these results that in the highly concentrated solutions the proportion of sulphur in sulphide form is very largely increased over that formed in the solutions prepared in open vessels, as shown in Table I. It is a well-established principle that the pentasulphide is the highest possible polysulphide, and the reaction by which calcium pentasulphide is produced by the union of lime and sulphur (see Equation 1 above) yields only 80 per cent. of the total sulphur in sulphide form, whereas in solutions A_3, B_4, and C_3, the proportion of the total sulphur which is in this form is 95.95 per cent., 95.54 per cent. and 94.00 per cent. respectively. Hence in the preparation of these solutions some secondary reaction must take place, resulting in the change of a large part of the thiosulphate into polysulphide sulphur. Just what this secondary reaction may be is very difficult to determine. The following possible equations have suggested themselves:

$$(5)\ CaS_2O_3 + Ca(OH)_2 + 4S = CaS_5 + CaSO_4 + H_2O$$

$$(6)\ 2CaS_2O_3 + 3Ca(SH)_2 = 2CaS_5 + 3Ca(OH)_2$$

$$(7)\ CaS_2O_3 + 3H_2S = CaS_5 + 3H_2O$$

$$(8)\ 4CaS_2O_3 = CaS_5 + 3CaSO_4.$$

A reaction according to (8) appears to be very improbable, both from theoretical reasons and from the fact that it would produce much more calcium sulphate than we have ever found in such a mixture. A reaction according to (7) or (6) requires the previous formation of hydrogen sulphide or calcium sulphhydrate respectively, the production of either of which under the conditions of boiling these solutions seems highly improbable. Equation (5) seems, therefore, to represent the most probable reaction of those which have suggested themselves. The presence

of a larger proportion of sulphate sulphur in these concentrated solutions than was found in the dilute solutions boiled in open air also favors the supposition that the reaction by which pentasulphide is produced at the expense of thiosulphate is accompanied by the formation of calcium sulphate. The smaller proportion of sulphate sulphur in some of the more concentrated solutions seems to oppose this view, however. On the other hand, the analytical methods for distinguishing quantitatively between these several forms of sulphur compounds are not yet thoroughly perfected and it may be that this apparent objection to the reaction would be removed if more exact methods of analysis were available. In the absence of better analytical methods, these results are presented as the best obtainable, and the conclusions suggested as a possible step toward a better knowledge of the reactions between lime and sulphur under varying conditions.

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[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY.]

THE RELATIVE SOLUBILITY OF THE SILVER HALIDES AND SILVER SULPHOCYANATE.

BY ARTHUR E. HILL.

Received October 22, 1907.

The theory of electrolytic dissociation teaches that if saturated solutions of two very insoluble salts which have an ion in common could be mixed without increase of volume, precipitation of both salts would occur. For example, saturated solutions of AgCNS and AgCl would, upon mixing, precipitate both compounds in part, since by the addition of silver ion the solubility product of each salt would be exceeded. The quantities of chloride and sulphocyanate precipitated would be such as to leave the solution saturated in respect to both salts, and the equilibrium finally reached would be expressed for the respective compounds by the equations $C^{+}_{Ag} \times C^{-}_{CNS} = K_1$ and $C^{+}_{Ag} \times C^{-}_{Cl} = K_2$, where C stands for concentration in equivalents per unit volume, K_1 and K_2 are the products of the free ions (solubility products), and the subscripts denote the respective ions. By division,

$$\frac{C^{+}_{Ag} \times C^{-}_{CNS}}{C^{+}_{Ag} \times C^{-}_{Cl}} = \frac{K_1}{K_2} \qquad \text{(Equation 1).}$$

The common term C^{+}_{Ag} may be cancelled out, the relation becoming

$$\frac{C^{-}_{CNS}}{C^{-}_{Cl}} = \frac{K_1}{K_2} \qquad \text{(Equation 2).}$$

The same equilibrium will be attained if to a solution of AgCl, in presence of excess of the salt, a *soluble* sulphocyanate, such as KCNS, be added in sufficient quantity to exceed the solubility product of AgCNS. Precipitation of AgCNS will result, reducing the concentration of silver ions; the solution will therefore become temporarily undersaturated with respect to AgCl, and the latter salt will dissolve, thereby increasing the concentration of chloride ions and also of silver ions, so that the cycle of reactions will again be set in operation. Simultaneous precipitation of AgCNS and solution of AgCl will continue until the mixture contains the ions $\overline{Cl}$ and $\overline{CNS}$ in such quantities as are in equilibrium with the two silver salts, as expressed in equations 1 and 2. The solution thus obtained differs from the hypothetical solution discussed in the preceding paragraph in having present an additional cathion (potassium ion) and in having the chloride and sulphocyanate ions present in amounts measurable by ordinary analytical methods. The theory of solution equilibria of this character was first stated by Nernst.[1]

By the application of equation 2 to reactions such as the foregoing it becomes possible to determine the relative solubility of two difficultly soluble salts whenever (1) the concentration of the free ions ($C_{\overline{CNS}}$ and $C_{\overline{Cl}}$ in the example given) can be calculated from the total concentration of the substances in the solution as analytically determined, and (2) the degree of dissociation of the two insoluble salts in saturated solution is known, so that the total solubility can be calculated from the solubility products (K_1 and K_2). Following this method a number of such equilibria have been investigated, and the solubility of the salts determined. Guldberg and Waage's classic results on the reaction $BaCO_3 + K_2SO_4 = BaSO_4 + K_2CO_3$ have been shown by Nernst[2] and by Meyerhoffer[3] to refer to an equilibrium of this class, although originally interpreted otherwise. Other investigators have studied the following reactions of this type:

$$TlCl + KCNS \rightleftharpoons TlCNS + KCl \text{ (Knüppfer[4])}.$$
$$PbI_2 + Na_2SO_4 \rightleftharpoons PbSO_4 + 2NaI \text{ (Findlay[5])}.$$
$$CaCO_3 + K_2C_2O_4 \rightleftharpoons CaC_2O_4 + K_2CO_3 \text{ (Foote[6])}.$$
$$2AgCl + 2KOH \rightleftharpoons Ag_2O + 2KCl + H_2O \text{ (Noyes and Kohr[7])}.$$
$$BaC_2O_4 + CaCl_2 \rightleftharpoons CaC_2O_4 + BaCl_2 \text{ (Foote and Menge[8])}.$$

[1] "Theoretische Chemie," 5th edition, p. 535.
[2] "Theoretische Chemie," 5th edition, p. 535.
[3] Z. physik. Chem., 53, 513 (1905).
[4] Ibid., 26, 255 (1898).
[5] Ibid., 34, 407 (1900).
[6] Ibid., 33, 740 (1900).
[7] Ibid., 42, 336 (1902). This Journal, 24, 1141 (1902).
[8] Am. Chem. J., 35, 432 (1906).

$$BaCO_3 + CaCl_2 \rightleftharpoons CaCO_3 + BaCl_2 \text{ (Foote and Menge).}$$
$$BaF_2 + CaCl_2 \rightleftharpoons CaF_2 + BaCl_2 \text{ (Foote and Menge).}$$

The investigation here described has as its object the study of the relative solubility of the silver halides and silver sulphocyanate by means of the solution equilibrium discussed above. The reactions studied were the following:

$$AgCl + KCNS \rightleftharpoons AgCNS + KCl.$$
$$AgCNS + KBr \rightleftharpoons AgBr + KCNS.$$
$$AgBr + KI \rightleftharpoons AgI + KBr.$$

The series seemed worthy of investigation both because of the value of additional data on the solubility of these important silver salts and further because the reactions appeared to be particularly well adapted to the method. The degree of dissociation of the four potassium salts was calculated from electrical conductivity data;[1] the values were found to agree within 1.8 per cent. in fifth-normal, 0.6 per cent. in twentieth-normal, and 0.1 per cent. in hundredth-normal solutions, and the salts may therefore be regarded as equal in dissociation. (As will be seen from what follows, the small error introduced by this assumption of equality is reduced by the extraction of the square roots in equation 4.) Since salts of equal dissociation constant having a common ion become equally dissociated when mixed in any proportions,[2] it follows that the ratio of the free ions (Equation 2) will be the same as that of the total chloride and sulphocyanate present, as analytically determined. Equation 2 then becomes

$$\frac{C_{\text{SULPHOCYANATE}}}{C_{\text{CHLORIDE}}} = \frac{K_1}{K_2} \qquad \text{(Equation 3),}$$

in which the subscripts denote total concentration. Furthermore, the four silver salts have been shown by Böttger[3] to be completely dissociated in saturated solutions, so that the ratio of the products of the ionic concentrations, $\frac{K_1}{K_2}$, becomes the ratio of the squares of the actual solubilities of the salts, $\frac{S^2_{AgCNS}}{S^2_{AgCl}}$. By substitution of this value for $\frac{K_1}{K_2}$ in equation 3, and extraction of the square roots, the relation becomes

$$\frac{S_{AgCNS}}{S_{AgCl}} = \frac{\sqrt{C_{\text{SULPHOCYANATE}}}}{\sqrt{C_{\text{CHLORIDE}}}} \qquad \text{(Equation 4),}$$

that is, the ratio of the solubilities of the two salts is equal to the ratio

[1] Landolt-Börnstein-Meyerhoffer, Tabellen, 3rd edition, p. 744.
[2] Nernst's "Theoretische Chemie," 5th edition, p. 509.
[3] Z. physik. Chem., 46, 602 (1903).

of the square roots of the total concentrations of anions, free and combined. This simple relation renders unnecessary the corrections for inequalities in dissociation which have been applied in all the previously noted studies on solution equilibria except that of Knüppfer, thereby freeing the results from that source of possible error. In one particular only does the series fail of the ideal for an investigation of this character—the solubilities are in two cases widely divergent, so that small errors in analysis would cause noticeable variations in the ratios found. It has been possible, however, to reduce these errors to such an extent that they do not greatly affect the constancy of the ratios obtained.

The silver salts used in the experiments were prepared by precipitating pure silver nitrate in hot dilute solution with excess of the haloid salt, and washing the precipitates by decantation until the wash waters were free from halogen. The silver chloride was dissolved in ammonia, reprecipitated by nitric acid and again washed by decantation. All the silver salts were kept in a moist condition and protected from the light. The potassium chloride and sulphocyanate were Kahlbaum's C. P. preparations, and the latter was found by analysis free from chloride; the potassium iodide and bromide were Baker & Adamson's analyzed preparations, the iodide containing 0.005 per cent. and the bromide a mere trace of chloride.

The reactions were carried out in half-liter flasks suspended in an Ostwald thermostat regulated to 25°, and the reaction mixtures stirred by glass paddles operated by a gas engine. In each experiment a solution of the potassium salt of approximately the desired concentration was taken, and about twice its equivalent of the moist silver salt added to it. The mixture was stirred for about two hours, after which a further quantity of the silver salt was added and the stirring continued two to four hours longer. The time thus allowed was considerably greater than was necessary, as the reactions are apparently very rapid in all cases; equivalents of AgCl and KCNS have previously been shown[1] to react to the extent of about 43 per cent. in two minutes in solution of hundredth-normal concentration. Further experiment on this reaction showed that the equilibrium was reached in less than one hour; the velocity of the other reactions was not investigated. After equilibrium had been reached, the solutions were allowed to stand in the thermostat until the precipitates had settled and samples were then pipetted out and analyzed. Each equilibrium was approached from two directions. The concentration of the potassium salt was varied through a considerable range, so that any irregularity in the ratios, due to hydrolysis or the formation of complex salts, might be noticed. The constancy of the ratios shows that no

[1] Rosanoff and Hill, This Journal, 29, 272 (1907).

measurable irregularities occur within the range of concentrations selected, and that the assumptions leading to equations 3 and 4 are justified.

Table I shows the results obtained for the equilibrium AgCl + KCNS $\rightleftharpoons$ AgCNS + KCl. The solutions were analyzed for total chloride and sulphocyanate by the method of Volhard,[1] and for sulphocyanate by the colorimetric method, the chloride being determined by difference. For the Volhard determination 25 cc. samples were taken in experiments 1*a* and 1*b*, 50 cc. samples in 2*a* and 2*b*, and 100 cc. samples in 3*a* and 3*b*. For the colorimetric tests the standards were made in every way identical with the analyzed solutions by mixing solutions of potassium chloride and potassium sulphocyanate in such quantities that the total salt in the standard was equal to that in the sample tested, and by adding equal quantities of iron-ammonium alum to the two solutions. In the following table, column 1 gives the number of the experiment, column 2 the approximate concentration of the soluble salt used, column 3 the salts taken for the reaction, and columns 4 and 5 the final concentration of chloride and sulphocyanate as analytically determined. Column 6 gives the ratio of the square roots of these concentrations, which, according to equation 4, is equal to the ratio of the solubility of the two salts.

TABLE I.

Equilibrium AgCl + KCNS $\rightleftharpoons$ AgCNS + KCl at 25°.

No.	Approx. concen.	Reacting salts.	Conc. Cl.	Conc. CNS.	$\sqrt{\frac{C_{CNS}}{C_{Cl}}}$
1*a*	N/5	AgCNS + KCl	0.197	0.00104	0.0726
1*b*	N/5	AgCl + KCNS	0.193	0.00100	0.0719
2*a*	N/20	AgCNS + KCl	0.0501	0.000293	0.0764
2*b*	N/20	AgCl + KCNS	0.0489	0.000280	0.0759
3*a*	N/100	AgCNS + KCl	0.010	0.000060	0.0774
3*b*	N/100	AgCl + KCNS	0.010	0.000057	0.0750

Mean ratio, $\frac{S_{AgCl}}{S_{AgCNS}} = 0.0748$

TABLE II.

Equilibrium AgCNS + KBr $\rightleftharpoons$ AgBr + KCNS at 25°.

No.	Approx. Concen.	Reacting salts.	Conc. Br.	Conc. CNS.	$\sqrt{\frac{C_{Br}}{C_{CNS}}}$
1*a*	N/5	AgCNS + KBr	0.0647	0.1205	0.732
1*b*	N/5	AgBr + KCNS	0.0665	0.1207	0.742
2*a*	N/20	AgCNS + KBr	0.0165	0.0312	0.727
2*b*	N/20	AgBr + KCNS	0.0176	0.0324	0.737

Mean ratio $\frac{S_{AgBr}}{S_{AgCNS}} = 0.735$

[1] J. pr. Chem., 9 (N. F.), 217 (1874). See also this Journal, 29, 269 (1907).

Table II shows the results obtained by comparing AgBr and AgCNS. The solutions were analyzed for bromides by the method of Rosanoff and Hill,[1] the total bromide and sulphocyanate being determined by the method of Volhard. The columns have the same significance as in the previous table.

Attempts were made to carry out experiments in solutions of hundredth-normal concentration, but fine suspensions of the silver salts resulted, which would not settle in reasonable time and could not be filtered out. The solutions were finally analyzed in the presence of the suspended solid, but under those conditions the results obtained by approaching the equilibrium from the two directions differed by 4 to 5 per cent., the amount of bromide in solution being larger when silver bromide had been taken than when its original source was the soluble potassium bromide. The values for the ratio were 0.0709 and 0.0700 when silver sulphocyanate was the original solid phase, and 0.0787 and 0.0763 when silver bromide was taken; the mean is almost identical with that of Table II. Whether this peculiarity is referable simply to analytical errors due to the presence of the finely suspended silver salts or, as seems to be indicated by Table II, to some change in the nature of the solid phase (mixed crystals, solid-solution, or the like) must remain for the present unanswered.

Analytical difficulties prevent the determination of the relative solubility of silver iodide and bromide from being as accurate as might be desired. The iodide in solution when equilibrium has been attained amounts to only 0.01 to 0.02 per cent. of the bromide present, expressed in equivalents, and no method is known by which such minute quantities of iodides can be exactly determined in the presence of such large amounts of bromides. Of the various methods proposed for this separation, that of Fresenius,[2] which depends upon the oxidation of the iodides by nitrous acid in sulphuric acid solution, extraction of the free iodine by means of an organic solvent and titration with $Na_2S_2O_3$, was thought to be best suited to the estimation of small amounts of iodine. Test analyses were made of solutions containing 0.1 to 0.5 mg. of iodide in presence of 2 to 3 grams of bromide dissolved in 150 cc. of water. The iodine freed by five drops of a solution of nitrous acid in concentrated sulphuric acid was collected by extraction of the aqueous solution with 10 cc. portions of chloroform until no further coloration of the solvent could be detected; the iodine was then titrated with N/400 $Na_2S_2O_3$. The quantity found was always less than that taken, and by amounts varying between 12 and 40 per cent. If this maximum error be assumed to have occurred in the analysis of the mixtures recorded in Table III, the error in the ratios calculated will be about 27 per cent., and the ratios

[1] This Journal, 29, 1461 (1907).

[2] Quan. Chem. Anal. (Braunschweig, 1898), p. 482.

given below may therefore differ from the true ratios by that amount. In the experiments tabulated below, somewhat greater concentrations were used than in the previous experiments, in order that the iodide present might become a measurable quantity.

TABLE III.

Equilibrium AgBr + KI ⇄ AgI + KBr at 25°.

No.	Approx. Concen.	Reacting salts.	Conc. Br.	Conc. I.	$\sqrt{\frac{C_I}{C_{Br}}}$
1*a*	N	AgI + KBr	0.955	$24.4 \times (10)^{-5}$	0.016
1*b*	N	AgBr + KI	0.945	$13.9 \times (10)^{-5}$	0.012
2*a*	N/5	AgI + KBr	0.185	$4.83 \times (10)^{-5}$	0.016
2*b*	N/5	AgBr + KI	0.187	$2.2 \times (10)^{-5}$	0.011

Mean ratio $\frac{S_{AgI}}{S_{AgBr}} = 0.014$

From the ratios recorded in Tables I, II and III the relative solubility of the whole series may be calculated. The values thus obtained are given in Table IV. Column 1 designates the salt, column 2 its relative solubility referred to that of silver chloride as unity, and column 3 the absolute solubility in gram-molecules per liter, taking Kohlrausch and Rose's[1] figure for the silver chloride as the standard. Column 4 gives the maximum and minimum values obtained for the solubility of these salts by other methods; the figures are taken from the table complied by Abegg and Cox.[2]

TABLE IV.

Salt.	Relative solubility.	Absolute solubility.	Extreme values.
AgCl	1.00000	$1.6 \times (10)^{-5}$	$1.25—1.64 \times (10)^{-5}$
AgCNS	0.07480	$1.2 \times (10)^{-6}$	$1.08—1.25 \times (10)^{-6}$
AgBr	0.05500	$8.8 \times (10)^{-7}$	$6.6—8.1 \times (10)^{-7}$
AgI	0.00077	$1.23 \times (10)^{-8}$	$0.97—1.05 \times (10)^{-8}$

The foregoing investigation is one of a series planned in collaboration with Professor M. A. Rosanoff. A change of residence has made it advisable to carry out the separate parts of the work independently. Credit is gladly given to Professor Rosanoff for many of the ideas contained in this paper.

NEW YORK UNIVERSITY,
October, 1907.

ON THE ANALYTICAL ESTIMATION OF GLIADIN.

BY WALTER E. MATHEWSON.

Received October 21, 1907.

That the common methods for the determination of gliadin are unsatisfactory is generally recognized. The amount of nitrogenous material

[1] Abegg and Cox, Z. physik. Chem., 46, 11 (1903).

[2] *Loc. cit.*

extracted by dilute alcohol varies with the strength of alcohol used,[1] the relative proportion of alcohol to the flour,[2] and with the relative amounts of certain non-nitrogenous constituents of the latter, as acids[3] and salts. The experiments described here were carried out in the hope that a better procedure might be devised than that ordinarily followed. Five of the flour samples used were patent flours milled in the Experiment Station with the Experimental Roller Reduction Mill by Mr. C. O. Swanson. They had been bolted through No. 10 and No. 12 cloth. The sixth sample (No. 6) was a patent flour from the Manhattan Milling Company.

All alcohol used had been redistilled before use and was perfectly neutral to sensitive litmus paper. The concentrations given are by weight, not by volume. The alcohol, phenol, etc., used in the nitrogen determination were tested by blanks and the phenol was also examined for optical activity. All extractions were made in duplicate, the maximum difference allowed on the nitrogen determinations being 0.03 per cent. The results are expressed in terms of crude gliadin, obtained by multiplying the nitrogen found in the extract by 5.7. No attempt was made to correct for the amides present, since the values obtained in this determination are so largely dependent upon the protein precipitant used.[4] They could have been present only in very small amount, as the flours were sound and fresh. All percentages given are based upon the air-dry substance. The validity of the views of Osborne and Voorhees regarding the wheat proteins is assumed throughout the discussion.[5]

Below are given the percentages of moisture, crude protein (nitrogen × 5.7), and crude gliadin of the samples as determined in one of the usual ways; namely, by extracting 4 grams of the charge with 100 cc. cold 70 per cent. alcohol in a tight bottle, filtering, and determining nitrogen in 50 cc. of the filtrate. In the last column are given the results obtained when 16 grams of flour to 100 cc. of alcohol were taken.

No. of Sample	Moisture.	Total crude protein.	Crude gliadin. 4 grams flour, 100 cc. alcohol.	Crude gliadin. 16 grams flour, 100 cc. alcohol.
1	11.20	11.42	6.00	5.08
2	11.70	7.21	3.72	3.19
3	11.23	11.20	5.56	4.90
4	10.90	11.17	5.92	5.34
5	11.52	12.61	6.75	5.93

To guard as far as possible against incomplete extraction the mixtures

[1] Teller, Bull. Ark. Expt. Sta., No. 53, p. 63.

[2] Chamberlain, Bull. Bur. Chem., U. S. Dept. Agr., p. 125, No. 90. Chamberlain, This Journal, 28 (1906), 11, p. 1660.

[3] Snyder, Annual Rept. Minn. Expt. Station, 1904, p. 206.

[4] Schulze, Landw. Vers.-Sta., 26, 213 (1881).

[5] Osborne and Voorhees, Am. Chem. J., 15, 392 (1893).

were allowed to digest about forty-eight hours before filtration, being begun in the afternoon and frequently shaken until evening and during the next day. The fear that any gliadin would be coagulated by prolonged contact with 70 per cent. alcohol seems to the writer to be entirely unfounded, as pure gliadin prepared by Osborne's method, dissolves completely in alcohol of this concentration and the solutions remain clear for weeks, perhaps indefinitely. Nor would one anticipate that the error due to solution of nitrogenous matter not gliadin would be increased much relatively by the standing during the second day.

Sample No. 6 when treated with varying amounts of solvents gave the following results:

Grams flour per 100 cc. alcohol.	Per cent. crude gliadin.
1	4.57
2	4.39
4	4.37
8	4.29
16	4.22

The lower results obtained when the larger quantities of flour are used may be due both to less complete extraction and to the solution of non-gliadin nitrogenous substances, which dissolve but slightly and in more or less constant amount.

Gluten appears to be a solid colloid solution containing essentially the two gluten proteins with water. It would seem possible that a certain amount of gliadin might be held in solution in the glutenin, tending to divide itself between the two phases according to the distribution law. To test this a solution of pure gliadin in alcohol of about 60 per cent. was prepared. It gave a rotation of 21.6° Ventzke in a 200 mm. tube in a triple shadow saccharimeter. Twenty-five cc. of this solution were added to 5 grams of gliadin-free, dried flour prepared from sample No. 6 by repeated extraction with dilute alcohol, washing with concentrated alcohol and drying. The mixture was shaken frequently for three or four hours, allowed to stand over night, filtered and the filtrate polarized. A sample of the gliadin solution was also filtered under the same conditions, as a check to determine possible loss by evaporation under these conditions, and another sample of the flour was digested in the same way with 70 per cent. alcohol, to make sure that optically-active, alcohol-soluble substances had been removed. The gliadin solution was found to have suffered no change in concentration that could be detected with the saccharimeter, by contact with the flour. A second experiment was carried out in exactly the same way except that instead of flour, 5 grams of air-dry, pulverized crude glutenin were used, this being prepared by treating thoroughly washed gluten, cut into small pieces in a meat cutter, with successive portions of dilute alcohol for some time. It was then

washed with strong alcohol, allowed to dry at room temperature, ground to a powder that would pass through a 1 mm. mesh sieve, and this extracted in an extraction apparatus with ether and with absolute alcohol. After repeatedly extracting again with dilute alcohol, it was rinsed with strong alcohol and dried at room temperature.

The crude glutenin swelled up in the gliadin solution, but after applying the small correction for increase in concentration on filtration, the rotation was found to have increased from 10.8° V. to 12.1° V. Instead of removing gliadin from the solution the glutenin had evidently taken up water or dilute alcohol, thus increasing the rotation of the liquid. If glutenin had a marked tendency to hold gliadin in solution one would hardly expect this result.

As has been shown conclusively by Chamberlain[1] dilute alcohol dissolves other protein substances from flour beside Osborne's gliadin. Gliadin dissolves most readily in alcohol of about 70 per cent. (by volume), but a weaker alcohol dissolves a considerably larger percentage of nitrogenous matter from flour. Had we some method of rendering this foreign protein matter insoluble before the extraction, without affecting the gliadin, it would remove one of the most important sources of error. It was thought by the writer that possibly this could be effected by heat. A sample of pure gliadin was heated for six hours in an ordinary drying oven surrounded by boiling water. It did not seem to be changed physically and dissolved to a perfectly clear solution on warming somewhat with dilute alcohol, the solution remaining clear on cooling. Nor did gluten made from flour heated in the same way appear to differ much either in properties or amount from that made from similar flour which had not been heated. According to Osborne, leucosin, the albumen of wheat, is coagulated at temperatures of about 55–65°. The globulin is partially coagulated at 100°. Proteoses and amides are present in very small amount.

Below are given the results obtained by extraction with 70 per cent. alcohol after previous heating for five hours in an oven surrounded by boiling water. In the first column are given the results obtained by treating with cold alcohol (100 cc. for 4 grams) in the ordinary way.[2] In the second set of determinations the same proportion of flour and solvent were used, but the bottles were maintained at a temperature of 60–70° for about four hours during the digestion, the hot mixture being frequently shaken. As in the other determinations the flour remained in contact with the alcohol about forty-eight hours, during 12 to 14 of which the mixture was frequently shaken.

[1] Chamberlain, This Journal, 28, 1661 (1906).

[2] The much lower results obtained by Chamberlain are doubtless due in large measure to the difference in time allowed for extraction.

No. of sample.	Crude gliadin, cold extraction.	Crude gliadin, hot extraction.
1	4.97	5.62
2	3.24	3.60
3	4.78	5.46
4	5.30	5.85
5	5.94	6.66

As there seemed some danger that the glass-stoppered digestion bottles might not altogether prevent the loss of alcohol during the heating, they were weighed at the beginning and the close of the digestion. The highest loss was 0.3 gram, most of them not having lost half this amount.

In the opinion of the writer it is impossible to obtain satisfactory results by washing a flour repeatedly on a filter with hot alcohol of the usual concentration. A filter that will retain the fine suspended matter cannot act rapidly and in the washing, it is practically impossible to prevent losses of alcohol from the solvent, as a result of which it is enabled to dissolve more protein.

The percentages of gliadin found by the cold extraction of the dried flour are likely too low, the strongly dried protein going into solution very slowly in the cold solvent. The amounts dissolved in the hot extraction are almost as high as those given by cold alcohol on air-dry flour. If a purer gliadin was dissolved after the heating, the tendency to higher results by the ordinary method must be more or less offset by incomplete extraction.

It was thought that perhaps dilute *n*-propyl alcohol might prove a suitable solvent for the separation of gliadin. Seventy per cent. propyl alcohol is a mixture of constant boiling-point (about 86°) and hence can be used in an extraction apparatus. Seventy per cent. propyl alcohol dissolves pure gliadin with some difficulty when cold, but readily when hot. The results given below were obtained by using the solvent in a percolating extractor, the 2-gram charge of flour being held in a S. and S. filter paper shell. The liquid in the flask was kept rapidly boiling to bring about as rapid an extraction as possible.

No. of sample	Duration of extraction, hours.	Percentage crude gliadin.
1	10	5.99
2	5	3.66
3	10	5.51
4	10	6.27
5	10	6.18

The figures indicate no special advantage over the preceding methods.

Anhydrous phenol dissolves gliadin readily and apparently without affecting it chemically.[1] Further, pure phenol has a comparatively limited power as a solvent, and gliadin has a high specific rotation in this

[1] This Journal, **28**, 1483 (1906).

liquid. Mixtures of flour with phenol are difficult to filter and in making the experiments described below this was accomplished by using a Gooch crucible with asbestos felt. The filtering tube containing the crucible was connected with a 100 cc. distilling flask which served as the filtering flask. The pump was turned on and the mixture poured on the felt. A good vacuum was almost at once produced in the little filtering flask. A pinchcock was then placed on the rubber tube leading to the pump and, the apparatus being tight, it was not usually necessary to exhaust it again. The Gooch crucible was covered with a watch-glass and surrounded by a block-tin coil, through which steam could be passed to keep its contents from congealing. With this arrangement the filtrations could be made without any perceptible loss of solvent. Ten-gram charges of the flour were weighed out, dried and extracted with accurately measured volumes of phenol (96 cc. for sample one, 100 cc. for the others), the mixtures being kept at about 40° and frequently shaken for the first three or four hours. After about twenty-four hours they were filtered. Nitrogen was determined in an aliquot part by placing it in a Kjeldahl flask, adding about 300–400 cc. of water, 2 cc. of concentrated sulphuric acid and a little granulated zinc. It was then boiled until only a few cubic centimeters remained, the water vapor carrying off practically all the phenol, but the sulphuric acid preventing any loss of nitrogen as was indicated by the concordance of duplicates. Sulphuric acid was then added and the determination carried out in the usual way. In calculating the percentage of crude gliadin from the polariscope readings the optical rotation of gliadin was taken $[\alpha]_D^{40^\circ} = 132^\circ$.

CRUDE GLIADIN EXTRACTED BY ANHYDROUS PHENOL.

No. of sample	Crude gliadin calculated from nitrogen determination.	Crude gliadin calculated from polariscope reading.
1	9.86	8.08
2	6.19	4.83
3	9.43	7.93
4	7.12	6.39

The high results and differences between the percentage of crude gliadin as determined by polarization and by the nitrogen determinations show the presence of another protein or proteins largely soluble in phenol. The alternative is that dextro-rotatory substances were also present in the extract. Portions of the latter from samples 2 and 3 were taken, treated with one-fifteenth their volume concentrated sulphuric acid and the gelatinous precipitates filtered off. Both filtrates seemed to contain a trace of dextro-rotatory substance, but in so small amount that its presence could not be demonstrated with certainty—certainly less than would correspond to 0.4 per cent. protein in the flour. Duplicate nitrogen determinations were made on the filtrate from No. 4; it was free from

nitrogen. It is unlikely that any carbohydrate-like substances that might have been dissolved in the phenol would have been precipitated by the sulphuric acid. Gliadin solutions in phenol give no precipitate with phenol solutions of mercuric iodide or of iodine.

The above facts taken in connection with the fact that the gliadin apparently remains unchanged in phenol are of some interest because the view has been advanced that gliadin is formed by the action of dilute alcohol on the wheat, being split off from some other protein substance. The high percentage of protein removed by the phenol evidently includes another protein or other proteins in considerable quantity. An attempt to gain more data regarding this was made by extracting flours with dilute alcohol until the washings were practically free from protein. By this washing any dextro-rotatory substances soluble in dilute alcohol would also be removed. These samples were then dried and extracted with anhydrous phenol, the nitrogen content and the rotation of the extract determined. The amounts of protein dissolved were too small to enable accurate estimations to be made, but in both cases the crude gliadin, as calculated from the rotation, was not 60 per cent. of that obtained by multiplying the nitrogen by 5.7.

What other substances beside gliadin are dissolved by the phenol has not been determined. No careful experiments in this direction have been made, but the common animal proteins do not seem to be dissolved by it. Witte's peptone dissolves readily. The extremely weak acid character of phenol (its dissociation constant being not more than one two-hundredth that of carbonic acid) hardly leads one to suspect that it acts similarly to the strong acids on the other wheat proteins. In fact an alcoholic solution of phenol has been advocated as a quantitative protein precipitant.[1]

It might seem likely that besides the gliadin but one other wheat protein dissolves in phenol. Amides and proteoses are present in very small amount and it is doubtful if the former are soluble. If x represents the true percentage of gliadin in a flour and but two proteins are present in the phenol solution, then the specific rotation of the second protein in phenol would be:

$$[\alpha]_D^{40} = \frac{(\text{crude gliadin calculated from rotation of extract} - x)}{(\text{crude gliadin calculated from nitrogen of extract}) - x} \cdot 132$$

regardless of whether the extraction of the second protein were complete or not. The great influence of small experimental errors on this ratio renders it of comparatively little value, but in no case do the percentages of gliadin by a given method, when substituted for x, give concordant values for $[\alpha]$ for the four samples.

[1] Jago, Science and Art of Bread-making, p. 585.

Air-dry flour treated with phenol yields mixtures so difficult to filter that they were not investigated. Single extractions made with samples 2 and 3 gave the following values which, though not accurate, show that the protein dissolved from the air-dry flour is not pure gliadin.

No. of sample.	Crude gliadin calculated from nitrogen determination.	Crude gliadin calculated from polariscope reading.
2	5.24	4.15
3	7.80	6.43

The filtration of the extract was so slow that it may have changed more or less in concentration from evaporation or absorption of water.

Summary.

With these flours 8 to 17 per cent. more nitrogenous matter was extracted when 4 grams per 100 cc. of the solvent was used than when four times as much flour was taken.

After drying six hours in the water oven, 10 to 20 per cent. less gliadin was obtained by extracting with cold solvent. With the hot solvent the figures were nearly the same, being slightly lower. Pure gliadin remains soluble in dilute alcohol after the same treatment.

No tendency for glutenin to remove gliadin from its alcoholic solutions by absorption or with the production of a solid solution could be demonstrated.

Propyl alcohol of constant boiling-piont (70 per cent. by weight) used in an extraction apparatus gave results probably no more accurate than the others.

Anhydrous phenol dissolves a high percentage of protein matter from the flour. The dissolved matter is not pure gliadin, however, nor does it seem to consist of gliadin with but one other protein.

I acknowledge with pleasure and gratitude the encouragement I have enjoyed from Prof. J. T. Willard in making these experiments, also my indebtedness to Mr. C. O. Swanson for much valuable data concerning the samples.

KANSAS STATE AGRICULTURAL COLLEGE,
October 18, 1907.

THE EFFECT OF NITROGEN PEROXIDE UPON WHEAT FLOUR.

BY F. J. ALWAY AND R. M. PINCKNEY.

Received September 17, 1907.

Studies on the bleaching of flour by means of the oxides of nitrogen have been published by Avery,[1] Ladd,[2] and Snyder[3] in this country, by

[1] This Journal, 29, 571 (1907).
[2] Bull. 72, N. D. Agr. Exp. Sta. (1906).
[3] Report on bleaching of flour.

Balland[1] and Fleurent[2] in France and by Brahm[3] in Germany. All these have recognized that there is no appreciable change in the chemical composition, but as to the effect of the nitrogen peroxide upon the acidity, the color, the absorption, the taste, the odor and the baking qualities there is little agreement.

The flours referred to in this article are the same as those described in a previous publication.[4] The unbleached flours of high grade had a more or less yellow tint, the intensity of coloration varying greatly. The lower grades of unbleached flour had a gray tint; the amount of yellow coloring matter in these, appeared to be about the same as that contained in the higher grades obtained from the same wheat. These unbleached flours when treated with liquids that are able to dissolve the fat, such as ether, chloroform, benzene and petroleum ether, gave yellow solutions which lost their color when exposed to the sunshine. The more yellow a flour was, the more yellow was the solution obtained from it. The bleached flours when treated with the same solvents gave more faintly yellow colored solutions or even colorless solutions, if the bleaching had been carried far enough. If the amount of nitrogen peroxide used had been excessive, the solution was yellow. The fat from unbleached flours obtained by evaporating the ethereal solutions was yellow, that from thoroughly bleached flours colorless and that from overtreated flours yellow or yellowish brown. The lower grades of flour did not have their gray tints weakened by bleaching, and many of the samples of bakers' grade appeared more unattractive in the bleached, than in the unbleached condition, the yellow tint of the latter partly obscuring the gray color.

The Effect of Bleaching upon the Acidity of Flour.—Forty-nine pairs of flours sent by mills having bleachers were tested, and of these, thirty-nine showed no difference in acidity between bleached and unbleached. In three pairs, the bleached flour was the less acid, the differences being 0.01, 0.02 and 0.04 per cent. In seven pairs, the bleached flour was the more acid, the difference being 0.01 per cent. in five cases and 0.03 per cent. in two cases. In the two bleached flours showing 0.03 per cent. higher acidity than the unbleached, the amount of nitrites, expressed as sodium nitrite, amounted to 4.4 and 10.0 parts per million of flour. In the five other cases the nitrites amounted to 18.8, 6.2, 6.2, 3.8, 6.2 and 3.1 parts per million of flour.

An unbleached flour was treated with different amounts of nitrogen peroxide. On the following day, the acidity was determined with the following results:

[1] Compt. rend., 139, 822 (1904).
[2] *Ibid.*, 142, 180 (1906).
[3] Versuchs-Anstalt des Verb. Deut. Müller (1904).
[4] Alway and Gortner, This Journal, 29, 1503 (1907).

	Experiment No.					
	1	2	3	4	5	6
Volume of nitric oxide used to each 1000 grams of flour (in cubic centimeters)	0.0	25	25	25	50	50
Acidity, per cent	0.05	0.05	0.05	0.05	0.05	0.05

Portions of another flour, treated with different amounts of nitrogen peroxide on October 16, 1906, were tested for acidity on February 18, 1907.

Number of experiment.	Volume of nitric oxide used to each kilogram of flour (in cc.)	Acidity. Per cent.
0	0	0.07
1	10	0.07
2	20	0.07
3	30	0.07
4	50	0.07
5	75	0.08
6	100	0.08
7	125	0.10
8	150	0.10
9	175	0.09
10	200	0.10
11	300	0.11
12	400	0.11
13	500	0.11
14	1000	0.15
Same flour bleached at mill		0.07

When the amount of nitric oxide used, did not exceed 50 cc. per kilogram of flour, there was no appreciable change in acidity. Larger amounts of the oxide caused an increase in the acidity.

Those investigators who have reported an increase in acidity due to bleaching, have probably experimented with "overtreated" flours.

No difference in absorption or in the strength of the gluten was found between bleached and unbleached flours.

Baking Tests of Bleached and Unbleaced Flours.—Loaves of bread were made from 23 samples of unbleached flours as well as from the corresponding 23 mill bleached flours. The samples came from 12 different mills and represented three grades, seven pairs belonging to the patent, ten to the straight, and six to the bakers' grades. The loaves were baked on four different days, along with a bakers' commercial product, in an oven heated with wood. The color, texture, odor, and taste of the two members of each of the 23 pairs were compared.

In all cases, the bleached flour gave the whiter loaf. No difference was detected in the texture, odor, or taste of any pair. The 23 loaves from the unbleached flours weighed 12,857 grams, while the 23 loaves from the bleached flours weighed 12,904. The volume of the 23 loaves from the unbleached flours was 42,851 cc., and from the other 23 loaves, 42,735 cc. In eight pairs the unbleached loaf was the heavier, in 14 pairs

the lighter, and in one of the same weight as the bleached. In twelve pairs the unbleached loaf was the larger, in ten pairs the smaller, and in one pair of the same size. The differences in weight and volume of the two members of any pair were small, and only such as might occur in the case of two loaves made from the same flour. In all cases, the two loaves were of practically the same size and weight.

Baking tests were made with samples of a flour that had been treated in the laboratory with different amounts of nitrogen peroxide.

	Number of flour.				
	1	2	3	4	5
Vol. of nitric oxide used per kilogram of flour (in cc.)....	0	50	100	150	250
Weight of loaf (in grams).....	545	541	533	544	534
Volume of loaf (in cc.).....	1919	1827	1981	2105	1981
Color of crumb.....	Almost white	Pure white	Pure white	Pure white	White

All five loaves were baked at the same time. All were of fine even texture, and, with the exception of the last, were of agreeable odor and flavor. No. 5 had a musty odor and taste, but was eatable.

In the case of two bakings, 1 and 2, all the loaves made from bleached flours contained nitrites, while in the cases of two other bakings, 3 and 4, none of the 14 loaves contained nitrites. In the case of the first two bakings, the average amount of nitrites was 0.8, while the average amount of nitrites in the flour from which the loaves were made, was 6.0 parts per million. There was no relation between the amount of nitrite in the flour and that in the resulting bread (as shown in the following table).

AMOUNT OF NITRITES IN BREAD MADE FROM BLEACHED FLOURS.

Number of baking.	Series number of flour.	Series number of loaf.	Parts per million of nitrite	
			in flour.	in bread.
I	5	4	3.4	1.1
I	6	6	4.4	0.6
I	10	7	3.1	1.6
I	11	10	18.8	0.6
I	16	12	2.5	0.8
I	24	14	3.1	0.9
I	25	16	2.8	1.6
I	26	18	8.8	0.2
II	35	20	4.4	1.9
II	40	22	6.2	0.8
II	41	24	10.0	0.2
II	46	26	3.7	0.8
II	47	28	12.5	0.9
II	50	30	3.4	0.2
II	51	32	3.1	0.4
II	55	34	6.2	0.8

Conclusions.

(1) The yellow color of flours is due to a very minute quantity of a colored substance which is contained in the fat. When the fat is removed, high-grade flours become white. Exposure to the sunlight or treatment with nitrogen peroxide changes the colored compound into one or more colorless compounds. Both the fat and solutions of the fat from thoroughly bleached flours are practically colorless. Overtreated (so-called "overbleached") flours have a yellow to brownish-yellow color, and the fat, as well as the solutions of the fat, from overtreated flours are also colored.

(2) Bleaching with nitrogen peroxide does not increase the acidity of flours, while overtreating them with the same agent does.

(3) Neither the absorption of a flour nor the expansion of its gluten is affected by bleaching.

(4) Bread made from bleached flours does not differ in weight, lightness, texture, odor or taste from that made from unbleached flours; it is, however, in all cases whiter, where high-grade flours are used. Low-grade flours, when bleached, produce bread with an uninviting color.

(5) Bleached flours sometimes yield bread containing nitrites and at other times bread free of nitrites. In all cases the amount of nitrites in the bread is much smaller than that in the flour.

(6) The quantity of peroxide may be so increased as to seriously injure the quality of the flour, but such a quantity at the same time unfavorably affects the color.

(7) Low-grade flours when bleached do not resemble patent flours in appearance.

(8) Many of the conflicting opinions in regard to the effect nitrogen peroxide has on wheat flour are to be attributed to the investigation of flours that had been "overtreated."

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THE POWER OF SODIUM NITRATE AND CALCIUM CARBONATE TO DECREASE TOXICITY IN CONJUNCTION WITH PLANTS GROWING IN SOLUTION CULTURES.[1]

BY OSWALD SCHREINER AND HOWARD S. REED.

Received October 23, 1907.

Investigations upon the nature and action of toxic agents upon organisms have shown that there is not always a simple relation between them. Although the harmful effect of the toxic agent upon the organism is the main factor in the problem, it is no less true that the organism exerts an

[1] Published by permission of the Secretary of Agriculture.

influence upon the toxic agent which may modify its action to a greater or less extent. The present paper reports the results of a study of the action of living plants upon solutions of toxic organic compounds with and without the addition of sodium nitrate, calcium carbonate and other substances.

It has been known for some time that the addition of a second solute to a toxic solution often decreases the toxicity of the solution. Krönig and Paul[1] found that the addition of hydrochloric acid and of halogen salts to solutions of mercuric bichloride decreased their toxicity. Kearney and Cameron[2] showed that the toxicity of sodium carbonate and of magnesium salts is greatly lowered or overcome by the addition of calcium salts to the solution. True and Gies[3] have demonstrated the same thing for mixtures of the salts of heavy metals with salts of the light metals. Pigorini[4] has shown that the toxicity of silver nitrate may be remarkably lowered by the addition of the poisonous sodium thiosulphate, although in this case there would be an actual chemical interaction between the toxic agents.

The question arises whether the presence and activity of the organism does not play a part in ameliorating the toxic conditions. Reed has pointed out in a recent article[5] that such an action appears to play some part in the observed antagonism between calcium and magnesium. In the present study particular attention was paid to the effect of the plant upon the toxicity of organic compounds with and without certain inorganic salts.

Wheat seedlings of uniform age and size were employed in all the experiments described in this paper. The seeds were germinated on perforated cork plates, which floated on the surface of a pan of water.[6] The water cultures were made by placing the solution to be used into salt mouth glass bottles having a capacity of 250 cc. Ten seedlings were inserted in the same number of notches cut in the edge of each cork in the manner described by Whitney and Cameron[7] and by Livingston.[8]

The water used in making solutions was taken from the laboratory still and shaken with washed carbon black. At the end of thirty minutes it was filtered and was then ready for use. This method of treating ordinary distilled water with an insoluble absorbent agent as described

[1] Z. Hyg., 25, 1 (1897).

[2] Report 71, U. S. Dept. Agr. (1902).

[3] Bull. Torr. Bot. Club, 30, 390 (1903).

[4] Atti. r. accad. Lin., Classe sci. fis. mat. nat. (5) 16 (1), 359 (1907).

[5] Ann. Bot., 21, 565 (1907).

[6] For details of the method by which the seedlings were grown, the reader should see Plant World, 9, 13 (1906), and Bull. 40, Bureau of Soils, U. S. Dept. Agr. (1907).

[7] Bull. 23, U. S. Dept. Agr. (1904).

[8] Plant World, 9, 13 (1906).

by Livingston[1] is found to give physiologically pure water, and appears to be generally applicable to physiological work.

In estimating the growth of the plants in different solutions, records were kept of the weight of the green tops and of the amount of water transpired. It was found, however, that for measuring the effects of the different compounds employed in these experiments the transpiration record was more useful than the green weight. This is undoubtedly due to the fact that in many cases the root growth was more affected than the top growth. This would seem to be a necessary consequence of the more intimate contact with the toxic agent and doubtless for this reason, the root has been a standard indicator of toxicity studies in plant physiology. It has been shown that transpiration is more nearly proportional to the growth of both roots and tops of wheat and is therefore a better indicator of the effect on the plant than the weight of the green tops. In Table IV both green weight and transpiration are given together with a photograph of the plants themselves, and a comparison of the three records will serve to illustrate this point.

The experiments which are to be described were designed to study the effect of various treatments in overcoming the action of some organic substances which the writers have shown to be toxic to plant growth.

The Effect of Root Oxidation and of Adding Pyrogallol.—It was shown that tyrosine lost its toxic properties as a result of oxidation incident to continued exposure to the air. The aqueous solution of tyrosine, which was perfectly colorless when first prepared, became dark brown upon standing in contact with the air for several months. The exact nature of the products of oxidation is somewhat in doubt, although it is probable that homogentisinic acid and other oxidation products of tyrosine are present. These oxidation products were favorable to plant growth. The same relation was shown by the action of the compounds neurine, choline, and betaine. Increased state of oxidation was accompanied by decreased toxicity. It is not to be presumed that increased oxidation of an organic compound always produces a decrease in toxic effects, but such a result undoubtedly follows in certain cases.

Experiments were performed in which certain organic compounds possessing known toxic properties were subjected to mild oxidation. It seems possible that beneficial changes might be brought about by oxidation. It has been shown by the work of Raciborski[2] that the roots of plants possess very definite powers of oxidation. The writers[3] have shown, furthermore, that the roots of wheat plants grown in soil extracts

[1] Bull. 36, Bureau of Soils, U. S. Dept. Agr. (1907).

[2] Bull. Acad. Sci. Cracovie. Math-nat. Cl., 1905, 338; Ibid., 668.

[3] J. Biol. Chem., 3, Proc., 24 (1907).

and synthetic nutrient solutions are capable of quite energetic oxidation.

Experiments were accordingly planned to show whether the solutions of organic compounds would be less toxic to a second set of plants by reason of the oxidation performed by the first set. Solutions of five different compounds were prepared in concentrations of 1,000, 500, 250, 100, 50, 25 and 1 part per million. Wheat seedlings were installed in these solutions and allowed to grow twelve to fourteen days and the toxic effects noted. The first set of plants were then removed, the water lost by transpiration restored, and second sets of wheat seedlings installed.

Table I shows that for three of the five substances the lowest concentrations causing injury to plants had been altered during the growth of the plants. The concentrations causing the death of the plants were the same for both the first and second sets of plants.

TABLE I.—SHOWING THE EFFECT OF PLANTS IN ALTERING THE CONCENTRATIONS AT WHICH INJURY WAS FIRST SHOWN IN VARIOUS TOXIC SOLUTIONS.

(p.p.m. = parts per million).

Solutions.	Lowest concentrations causing injury. First crop.	Second crop.
Arbutin	25 p.p.m.	Originally 500 p.p.m.
Cumarin	1 p.p.m.	" 100 p.p.m.
Cinnamic acid	25 p.p.m.	" 25 p.p.m.
Sodium cinnamate	100 p.p.m.	" 100 p.p.m.
Vanillin	50 p.p.m.	" 500 p.p.m.

It will be seen that the arbutin solution which originally contained 500 p.p.m. was so reduced in toxicity by the growth of the first set of plants that it was no more toxic than a fresh solution containing 25 p.p.m. of arbutin. When cumarin solutions were replanted, the solution originally containing 100 p.p.m. was no more toxic than a freshly prepared solution of 1 p.p.m. The cinnamic acid solution showed no apparent improvement when used the second time; it was thought that this might have been due to the acid properties of the compound. The experiment was accordingly repeated with sodium cinnamate, which was much less toxic to seedlings than was cinnamic acid, as was shown by True,[1] but the growth of the first set of wheat plants did not perceptibly alter the point of injury for the second crop. It would seem from this that the activities of the roots were not able to alter sufficiently the properties of cinnamic acid to change its toxicity to seedlings. The question whether the activities of the roots were not modified by the properties of the cinnamic acid in such a way that the ameliorating powers were lost, seems worthy of more careful study than we have been able to give it.

The toxicity of the vanillin solutions was likewise greatly reduced by the growth of one set of plants. A solution which had originally con-

[1] Am. J. Sci. (IV), 9, 183 (1900).

tained 500 p.p.m. of vanillin appeared to be no more toxic to the second set of plants than a freshly prepared solution containing 50 p.p.m. had been to the first set of plants.

The roots growing in the stronger solutions of vanillin oxidized some of the vanillin to a dark purple dye, which was deposited on the root, similar to the oxidation effects noticed when roots grow in solutions of α-naphthylamine, benzidine, etc. The point may be raised, and with some propriety, that the first set of plants absorbed and removed some of the toxic substances from the solutions. While this may be true, it is not probable that the amounts absorbed were sufficient to account for such differences as were noted in the case of arbutin, the concentration of which was so altered that the action of a solution originally containing 500 p.p.m. was no more injurious than that of a freshly prepared solution containing 25 p.p.m. That the concentration at which injury was manifested was altered, while that at which death occurred was not, is in accord with the assumption upon which the experiment was made. The roots which grew in the stronger solutions were soon seriously injured, hence any power they may have possessed to oxidize, or otherwise to ameliorate toxic conditions had a very limited time in which to act.

Without speculating too much upon the nature of the changes produced by the action of the growing plants, it may be pointed out that they appeared to alter materially the toxicity of three of the five solutions used. Although the plants undoubtedly absorbed some of the dissolved matter from the solutions through their roots, they accomplished a still greater reduction in toxicity by their activities in the solution. It would seem that the oxidizing powers of the roots are able to change some of the organic compounds into other compounds less toxic to plants.

The beneficial action of certain organic substances has been pointed out in various experiments described by Livingston[1] and by the writers[2] which showed, for example, that the addition of 500 p.p.m. of pyrogallol to an unproductive soil increased the growth of wheat plants 101 per cent. The addition of small amounts (2 to 10 p.p.m.) of pyrogallol or α-naphthylamine to the extract of an unproductive soil also has a very beneficial effect. Organic substances, like the ones mentioned, cannot be considered as plant nutrients; even if they were, the small amounts added would be insufficient to account for the results produced. Their action may be upon the plant itself, causing it to resist the toxic action of the soil extract, or else these substances, being quite active chemically, act directly upon the toxic substances in the solution.

It became of interest, therefore, to test the action of pyrogallol upon

[1] Bulls. 28 and 36, Bureau of Soils, U. S. Dept. Agr.

[2] Bull. 40, Bureau of Soils, U. S. Dept. Agr.

some substance which was known to have a decidedly toxic action upon plants. Cumarin was selected as the substance to be tried because it had a nearly neutral reaction in aqueous solution. Four cultures of wheat plants were set up in each of four solutions containing 75, 50, 25 and 5 p.p.m. of cumarin respectively, together with four cultures in distilled water. Half of the cultures received pyrogallol at the rate of 2 p.p.m. and the other cultures served as controls for comparison. The experiment ran ten days, and growth was measured by transpiration.

The plants grown in solutions of cumarin containing 75 p.p.m. were killed alike whether they contained pyrogallol or not. In 50 p.p.m. of cumarin the growth was only 36 per cent. of the control plants, but the addition of pyrogallol allowed a growth which was 82 per cent. of the controls. The solutions containing 5 p.p.m. of cumarin supported a growth which was 93 per cent. of the controls, and when pyrogallol was added the plants made a growth which exceeded the controls by 16 per cent. These results make it almost certain that pyrogallol had affected the toxic action of the cumarin.

Pyrogallol has no direct value as a nutrient substance for the higher plants, so far as known. Nevertheless, the growth of plants in the cumarin solutions was benefited in each case, and in the solution containing 5 p.p.m. of cumarin the growth of plants was distinctly better than in distilled water. This result would seem to indicate that the presence of the pyrogallol had not only been able to overcome the deleterious effect of the cumarin but also to bring about a slightly greater growth. From this it would appear that the presence of an organic compound possessing no value as a nutrient may aid the plants in overcoming toxic conditions.

The Effect of Adding Sodium Nitrate and Calcium Carbonate.—To study this matter further, experiments were made in which substances commonly used as fertilizers were added to solutions of organic substances which were known to have a marked toxic action upon wheat plants. Forty plants in four cultures were used for each concentration of the toxic agent employed. The fertilizer salts were added to two of the cultures and comparisons were made with the two which received no fertilizer material. Sodium nitrate and calcium carbonate were the two substances experimented with. The former is especially efficient in producing improved growth when added to toxic soil extracts, in fact it almost invariably produces increased plant growth when applied to soils or water cultures. Calcium carbonate is likewise efficient in improving growth and is found to be quite generally beneficial when applied with green manures which are known to contain a variety of organic compounds.

Solutions were prepared containing arbutin, cumarin and vanillin, making them up in the concentrations shown in Tables II and III. One

Fig. 1. Effect of calcium carbonate in overcoming the toxicity of cumarin. Plants grown in: (1) Cumarin solution 25 p.p.m.; (2) Cumarin solution plus 2000 p.p.m. $CaCO_3$; (3) Cumarin solution 10 p.p.m., (4) Cumarin solutionplus 2000 p.p.m. $CaCO_3$; (5) Cumarin solution 1 p.p.m.; (6) Cumarin solution plus 2000 p.p.m. $CaCO_3$; (7) Distilled water; (8) Distilled water plus 2000 p.p.m. $CaCO_3$.

Fig. 2. Effect of sodium nitrate in overcoming the toxicity of vanillin for the first and second crop of wheat plants. (1) First crop in vanillin solution, (2) Second crop in vanillin solution; (3) First crop in vanillin solution plus 100 p.p.m. $NaNO_3$ (4) Second crop in vanillin solution plus 100 p.p.m $NaNO_3$; (5) First crop in vanillin solution plus 2000 p.p.m. $CaCO_3$; (6) Second crop in vanillin solution plus 2000 p.p.m. $CaCO_3$. (7) Control in distilled water.

series of solutions served as controls, to another sodium nitrate was added at the rate of 100 p.p.m. of NO_3, to another series calcium carbonate was added at the rate of 2000 p.p.m., except that arbutin was omitted from this series. The arbutin cultures were allowed to grow for nine days, the cumarin cultures for eleven days, and the vanillin cultures for ten days.

Tables II and III show the comparative growth of wheat plants in various concentrations of the toxic substances and the effect of the inorganic salts upon them. The growth of control plants in pure distilled water is used as a basis for the comparison and represented as 100 in each case.

TABLE II.—EFFECT OF ADDING SODIUM NITRATE TO TOXIC SOLUTIONS. RELATIVE GROWTH MEASURED BY TRANSPIRATION.

(p.p.m. = parts per million).

No.	Solutions.	Relative growth. Without nitrate.	100 p.p.m. NO_3 added.
1	Control in distilled water	100	289
2	Vanillin, 500 p.p.m	25	34
3	" 100 "	53	184
4	" 25 "	80	238
5	" 10 "	126	246
6	" 1 "	132	271
1	Control in distilled water	100	...
2	Arbutin, 500 p.p.m	23	27
3	" 100 "	41	78
1	Control in distilled water	100	...
2	Cumarin, 100 p.p.m	dead	dead
3	" 50 "	47	53
4	" 10 "	66	105

TABLE III.—EFFECT OF ADDING CALCIUM CARBONATE TO TOXIC SOLUTIONS. RELATIVE GROWTH MEASURED BY TRANSPIRATION.

(p.p.m. = parts per million).

No.	Solutions.	Relative growth. Without carbonate.	With 2000 p.p.m. $CaCO_3$ added.
1	Controls in distilled water	100	209
2	Vanillin, 500 p.p.m	25	107
3	" 100 "	53	127
4	" 25 "	80	183
5	" 10 "	126	184
6	" 1 "	132	201
1	Controls in distilled water	100	...
2	Cumarin, 100 p.p.m	dead	dead
3	" 50 "	dead	dead
4	" 25 "	36	58
5	" 10 "	74	127
6	" 1 "	97	166

It is quite evident from a survey of the results that these inorganic salts had a beneficial action when added to the toxic solutions, the effect being more marked in the case of the weaker solutions. The plants which grew in the cumarin solutions containing 25 p.p.m. and less are represented in Fig. 1.

It may be noted that one of the toxic substances (vanillin) produced, in the lower concentrations, what is ordinarily interpreted as stimulation. The phenomenon of increased growth in the presence of weak poisons is quite general and has been worked out in much detail by Raulin,[1] Richards,[2] Ono,[3] and others. There can be little question but that the increased growth of the plants in the vanillin solutions was caused by some stimulating action of the vanillin upon the functions of the plants. Turning now to the column expressing the effect of the inorganic salts upon the vanillin, no stimulating effect will be noticed. None of the solutions containing vanillin plus an inorganic salt produced an effect upon growth greater than did distilled water containing only the inorganic salts. In other words, the stimulating effect of the toxic agent totally disappeared.

It would appear that the fertilizer salts either had an action upon the toxic organic substances ameliorating the conditions for the growth of plants, or that they acted upon the plants in such a way that increased growth was possible in spite of the presence of the toxic compounds. Further evidence on these points was gained from the results of replanting certain of the solutions. The vanillin solutions enumerated in Tables II and III received a second set of wheat seedlings after the first had been removed. The water lost by transpiration was restored by adding distilled water, and the plants were allowed to grow nine days. The behavior of the second set of plants indicated that the conditions for growth were on the whole, even better than those existing during the growth of the first set, except in the solution originally containing 500 p.p.m. vanillin, in which the plants were again killed. In the first crop the injurious effect of vanillin itself was primarily on the root development and this condition was largely ameliorated by the calcium carbonate and sodium nitrate when added to the vanillin solutions. In the second crop the root system was, generally speaking, much improved in all three series, including those without fertilizer salts, again showing that activities of the living roots were able in part to overcome the toxic agents.

In order to ascertain whether the growth of the plants was a correct indication of the presence of vanillin, the solution was submitted to a

[1] Ann. Sci. Nat. Bot. [V] 11, 91 (1869).
[2] Jahrb. wiss. Bot., 30, 665 (1897).
[3] Jour. Coll. Sci. Tōkyō, 13, 141 (1900).

chemical examination.[1] Fairly large amounts of vanillin were shown by this test to be present in the solutions originally containing 500 p.p.m. vanillin, while only traces could be found in the solutions originally containing 25 or 10 p.p.m. No vanillin could be demonstrated in any of the solutions in which calcium carbonate or sodium nitrate had been present. There had been a diminution and even a total disappearance of the toxic substance.

An additional experiment will be described for the purpose of giving a direct comparison between the growth of the first and the second set of plants in toxic solutions containing inorganic salts. Three different solutions were employed in this experiment: the first contained 100 p.p.m. vanillin; the second, 100 p.p.m. vanillin plus 100 p.p.m. sodium nitrate; the third, 100 p.p.m. vanillin plus 2000 p.p.m. calcium carbonate. A set of wheat plants was allowed to grow in each of these solutions for eight days. The growth of the plants was of the same general character as represented in corresponding treatments in Tables II and III. After removing the plants from these solutions the original volumes were restored by the addition of distilled water to replenish that transpired by the first set of plants, and a second set of seedlings was installed. Nothing was added to the solutions except the distilled water. At the same time a set of plants was installed in a new set of solutions, precisely similar in composition to the original set. Accordingly, the plants in the new solution represented a first crop in toxic solutions containing fertilizers, and the replanted set represented a second crop in the originally similar solutions. The plants in these solutions together with controls in pure distilled water were allowed to grow ten days. The relative growth of the plants in the various solutions is given in Table IV and the plants are shown in Fig. 2.

The numbers and order of the solutions in the table correspond to those of the plants shown in the figure.

It will be seen that the results of this experiment confirm those of preceding experiments in showing that the toxic properties were ameliorated both by the action of plant roots and by the presence of inorganic salts. Where the two agencies worked in conjunction, the growth of the plants was the best. The second crop showed the better growth in each

[1] The method used seems to have been first described by Moerk, Amer. J. Phar., 63, 572 (1892), and cited in Z. anal. Chem., 32, 242 (1893). It consists in decolorizing the vanillin solution (if necessary) with freshly precipitated lead hydroxide, then adding bromine water, drop by drop, until a slight excess is present. Ferrous sulphate is finally added until the maximum blue-green color is reached. The test was slightly impaired in solutions to which calcium carbonate had been added, by the yellow color formed with the reagents, but the presence of sodium nitrate does not interfere with the test. It was not found to be strictly quantitative although the amount of color produced was indicative of the approximate amount of vanillin present.

case, owing to the action of the plant roots and the inorganic salts during the growth of the first crop.

TABLE IV.—RELATIVE GROWTH OF THE FIRST AND SECOND SETS OF PLANTS IN SOLUTIONS CONTAINING 100 PARTS PER MILLION VANILLIN WITH AND WITHOUT CERTAIN INORGANIC SALTS.

(p.p.m. = parts per million).

No.	Solutions.	Relative transpiration.	Relative green weight of tops.
1	First crop in vanillin solution	45	100
2	Second crop in vanillin solution	93	103
3	First crop in vanillin solution + $NaNO_3$ 100 p.p.m	114	99
4	Second crop in vanillin solution + $NaNO_3$ 100 p.p.m	190	135
5	First crop in vanillin solution + $CaCO_3$ 2000 p.p.m	141	111
6	Second crop in vanillin solution + $CaCO_3$ 2000 p.p.m	166	100
7	Controls in pure distilled water	100	100

Another experiment upon the action of these fertilizers was performed, using arbutin as the toxic substance and growing two sets of plants in the solution. Two cultures, each containing 10 wheat plants, were made for each concentration of solution employed. Arbutin was shown to be decidedly toxic to wheat plants, killing at a concentration of 500 p.p.m. and injuring at 25 p.p.m. As before, sodium nitrate and calcium carbonate were added to the solutions. The set of solutions receiving sodium nitrate was accidentally lost before it was chemically examined for arbutin and, hence, does not appear in the records of the second crop. The growth of the plants in these solutions is shown in Table V where the figures represent the relative transpiration. The first crop grew eleven days, the second crop ten days.

TABLE V.—RELATIVE GROWTH OF WHEAT PLANTS IN ARBUTIN SOLUTIONS WITH AND WITHOUT CERTAIN INORGANIC SALTS. GROWTH MEASURED BY TRANSPIRATION.

(p.p.m. = parts per million.)

No.	Solutions.	Relative transpiration. First crop.	Relative transpiration. Second crop.
1	Controls in distilled water	100	100
2	Arbutin, 1000 p.p.m	23	28
3	" 500 "	27	36
4	" 200 "	41	71
5	" 100 "	45	94
6	" 50 "	80	125
7	" 1000 " + calcium carbonate 2000 p.p.m	31	37
8	" 500 " + " " 2000 "	51	84
9	" 200 " + " " 2000 "	56	74
10	" 100 " + " " 2000 "	70	148
11	" 50 " + " " 2000 "	92	154
12	Distilled water + " " 2000 "	109	147
13	Arbutin, 1000 p.p.m. + sodium nitrate 100 p.p.m	33	..
14	" 500 " + " " 100 "	53	..
15	" 200 " + " " 100 "	72	..
16	" 100 " + " " 100 "	83	..
17	" 50 " + " " 100 "	91	..
18	Distilled water + " " 100 "	146	..

It will be seen from these figures that the general order of results was the same here as in the preceding experiment where a second set of plants was grown in toxic solutions. In making the comparison it is of course necessary to use the growth in "replanted" distilled water as the basis of the comparison and not fresh distilled water, since all solutions used for second crops contained the waste products of the first crop. The second crop was in all cases better than the first. Where the calcium carbonate had been added to the lower concentrations of arbutin, the second crop was remarkably good. These results bear out the results of chemical tests to determine the presence of arbutin.

It was found that Pauly's[1] diazobenzene-sulphanilic acid reagent could be used as an indicator for arbutin. While it is only approximately quantitative it gave good indications. Pure standard solutions of arbutin are colored bright crimson by the addition of a few drops of diazobenzene-sulphanilic acid reagent. Weak solutions of arbutin, especially after the growth of plants, are strongly tinged with yellow. The results of the chemical tests made after the growth of the first and second crops are given in Table VI.

TABLE VI.—ARBUTIN REMAINING IN SOLUTION AFTER GROWTH OF FIRST AND SECOND CROP OF WHEAT.

(p.p.m. = parts per million.)

No.	Solutions.	Results of tests to indicate arbutin. After first crop.	After second crop.
1	Originally containing arbutin 1000 p.p.m.	abundant	moderate
2	" " " 500 "	abundant	moderate
3	" " " 200 "	moderate	weak
4	" " " 100 "	weak	trace
5	" " " 50 "	none	none
6	" " " 1000 " + $CaCO_3$, 2000 p.p.m.	abundant	weak
7	" " " 500 " + " 2000 "	moderate	weak
8	" " " 200 " + " 2000 "	weak	trace
9	" " " 100 " + " 2000 "	trace	none
10	" " " 50 " + " 2000 "	none	none

An inspection of these results shows that the calcium carbonate had the same action upon arbutin as the inorganic salts used in the previous experiment had upon vanillin. There had been a disappearance of arbutin from the solutions in which plants grew, but much more had disappeared from solutions containing the inorganic salt.

In regard to the question as to how the toxic substance was caused to disappear, three possibilities seem to present themselves: (1) The plants themselves absorbed part of the toxic substance and oxidized some of it; (2) the inorganic salts had a direct action upon the toxic substance; (3) the plants and inorganic salts working together had a direct or in-

[1] Z. physiol. Chem., 42, 508 (1904); *Ibid.*, 44, 159 (1905).

direct action upon the toxic substance. The first possibility was tested by the experiment already described in which a second set of plants was grown in the toxic solutions. It was there shown that the plants did have an ameliorating action, although they were only able to overcome the toxic substances in the lowest concentrations.

In connection with the second possibility, *viz.*, that the fertilizer substances had a direct action upon the toxic substance, the following experiment will be of interest. A solution containing 100 p.p.m. of vanillin was prepared; a portion of it received sodium nitrate equivalent to 100 p.p.m. of NO_3, another portion received calcium carbonate at the rate of 2000 p.p.m., and still another portion received both sodium nitrate and calcium carbonate. These solutions were then allowed to stand ten days. At the end of that time another set of solutions, exactly similar to the first, was prepared. They were compared by growing plants in them and using the growth of the plant as an indicator of the ameliorating action of the salts added. Four cultures comprising forty plants were used for testing each solution. It was thought that any action the inorganic salts might have had, would be shown by the growth of the plants in the solutions.

The results of the experiment are presented in Table VII.

TABLE VII.—EFFECT OF TEN-DAY ACTION OF SODIUM NITRATE AND CALCIUM CARBONATE ON THE TOXICITY OF VANILLIN SOLUTIONS. GROWTH MEASURED BY RELATIVE TRANSPIRATION. (p.p.m. = parts per million.)

No.	Solutions.	Solutions prepared at time of planting.	Solutions prepared ten days before planting.
1	Controls in distilled water	100	100
2	Vanillin, 100 p.p.m	63	56
3	" 100 " + $NaNO_3$, 100 p.p.m	127	100
4	" 100 " + $CaCO_3$, 2000 "	125	166
5	" 100 " + $NaNO_3$, 100 " + $CaCO_3$, 2000 p.p.m	225	215

From these figures it will be seen that the action of sodium nitrate was not the same as that of calcium carbonate. The latter produced beneficial effects which were appreciably increased when it stood in contact with the toxic solution for ten days. Sodium nitrate, on the contrary, did not show any increase in its ameliorating powers upon standing, in fact the solutions appeared to become somewhat poorer in both the cases in which sodium nitrate was allowed to stand. The results seem to suggest that calcium carbonate has the power to act independently in ameliorating the toxicity of vanillin, and the lack of ameliorating action of the sodium nitrate may be due to the formation of intermediate compounds having as great or greater toxicity than the original. These points seem worthy of further study.

Regarding the third possibility it might be said that the experimental data thus far obtained, go to show that the physiological activities of the plants were able to ameliorate the toxic conditions and also that the action of certain inorganic compounds in the solution is able to bring about some improvement due probably to direct action on the toxic substances, but far greater improvement is effected by the combined action of plants and inorganic salts. In other words, the plants and inorganic compounds working together are able to accomplish more in the way of destroying a toxic substance than either can do working alone. That such a substance as vanillin is actually destroyed, does not admit of doubt, if any conclusion is to be drawn from the experiments previously recorded. Whether the destruction of vanillin took place in the solution or within the cells of the wheat plants was not ascertained, but it probably took place in the solution. This may be safely inferred from the behavior of the plants. Vanillin itself has a very inhibitive action upon the growth of the roots of wheat seedlings in water cultures. All plants grown in vanillin solutions showed more harmful effects in the growth of roots than in the growth of tops. When, however, fertilizer ingredients were added in sufficient amounts to ameliorate distinctly the growth of plants, the roots made as good or better relative growth than the tops. (Fig. 2.)

Summary.

The activities of the plant roots are able to decrease the toxicity of organic compounds to a certain extent, provided the original concentration of the solution is below that able to cause death of the plants. It is probable that the oxidizing power of the root plays a greater or less part in the process of amelioration. The first set of plants may have absorbed directly some of the toxic material from the solutions, but the greatly diminished toxicity of the solutions as well as the formation of dyestuffs indicated that other changes had taken place.

The addition of certain inorganic salts to solutions of toxic organic compounds was distinctly beneficial to plant growth. That the inorganic salts and the physiological activities of the plant working together, had accomplished the destruction of toxic substances was shown by both plant growth and chemical tests.

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A STUDY OF THE CHANGES TAKING PLACE IN WHISKEY STORED IN WOOD.

BY C. A. CRAMPTON AND L. M. TOLMAN.

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This investigation was planned and begun by C. A. Crampton, F. D. Simons and A. B. Adams in the laboratory of the Bureau of Internal Revenue, in 1898, in order to obtain more definite information concerning the changes taking place in whiskey when stored in wood, in connection with internal revenue laws relating to the bonding of distilled spirits and the sale of the same under government stamp. The analytical work was completed and manuscript prepared under the direction of L. M. Tolman, with the co-operatian of L. M. Law, A. L. Sullivan, E. H. Goodnow and L. B. Forst.

Some work had previously been done in the laboratory by E. Richards upon the maximum quantity of solid matter that could be extracted from oak shavings by proof spirits.[1]

The experiment was conducted with the co-operation of a large number of whiskey distillers, who furnished the material, which was placed in bonded warehouses under the supervision of United States storekeepers.

Thirty-one barrels of new spirits were set aside at that time in as many different warehouses and from as many different distilleries, and a quart sample from each barrel was taken for analysis and sent to the laboratory. These packages were carefully sealed by the officer in charge, to prevent any possible accident to the contents. The gauge of each package was taken, and the condition of the barrel and the warehouse noted.

Each year for eight years during the bonded period, the seals on the packages were broken and a quart was taken for analysis. These samples were all set aside in glass containers and a complete chemical examination made in 1906, after all of the samples from the various packages had been received, except that the determinations of alcohol, solids, color and color soluble in ether were made each year as the samples were received.

When the chemical work was begun (1906), we had a series of nine samples from each of the thirty-one packages, all of which are exactly the same age, the difference between them being the length of time each had been kept in the barrel. Sample No. 1, or the new spirit, had been kept eight years in glass. Sample No. 2 had been stored one year in wood and seven years in glass. Sample No. 3 had been stored two years in wood and six years in glass, and so on, up to the last of the series, which

[1] Annual Report, Commissioner of Internal Revenue, for 1889, page 60.

had been stored eight years in wood. In the discussion of these samples they will be designated by the length of time they were stored in wood.

The first sample, which was taken from the barrel when it was placed in the warehouse and which represents the fresh distillate, will be spoken of as "new spirit," although, as has been said before, it is of exactly the same age as all of the other samples.

The objection to the plan of keeping the samples until all were collected before making the chemical analysis is that we must not take into account the changes taking place after the sample was placed in the bottle; but it seems evident from the chemical analysis of the samples that this factor, the change taking place in the glass, may be neglected, as the results obtained on the new spirits, which had been kept for eight years in glass, showed that practically no change had taken place.

The advantage of this mode of procedure can be readily seen when we consider to what extent the methods of analysis of spirts have changed in the last few years; the results would have been of little comparative value if they had been made by different methods and different analysts. Further, by making all the determinations at one time on the nine samples which make up a series, we are able to detect slight changes that might not have been noticed if the samples had been analyzed eight years apart by different methods and by different analysts. This is especially true in the determination of fusel oil, in which case a uniform method of analysis has made the results very satisfactory, showing the gradual increase taking place from year to year. Even if the method employed should later be shown to be faulty, the chief value of the results, which is that they are strictly comparable, will not be lost. In the fusel oil work a special effort was made to keep the conditions of analysis absolutely uniform for each period, so as to eliminate the effects of temperature, reagents, etc. All of the nine samples making up the series were started at the same time and carried through to completion by the same analyst. The results obtained by this plan are very remarkable, and would have been entirely impossible with the varying conditions to which they would have been subjected if they had been analyzed year by year. The same plan was followed with all of the other determinations, thus making it possible to show the very small differences which occurred.

Methods of Analysis.

The methods of analysis used were those of the Association of Official Agricultural Chemists, with the exception of the determination of fusel oil, which was made by the modified Allen-Marquardt method. It was found, however, after a large amount of experimental work which will be published later, that it was necessary with this method to change the

oxidizing solution used in order to obtain satisfactory results. The following solution was finally adopted: 5 grams of potassium bichromate, 5 cc. of concentrated sulphuric acid, the whole made up to 50 cc. with water.

It was also found that it was necessary to take smaller amounts of the whiskey for this determination on account of the high content of the fusel oil found in some cases, so that in all these determinations 50 cc. of whiskey were used instead of 100 cc., as given in the method.

The determination of the amount of color in the whiskies was made in a half-inch cell by a comparison with the standard glasses of the Lovibond colorimeter, using those of the brewer's scale, and the results are all reported in degrees of this scale referred to the half-inch cell.

The determination of amount of color removed by ether was made by the method of Crampton and Simons,[1] and results reported as per cent. of color removed.

The determination of the amount of color insoluble in water was made by the method of Walker and Schreiber,[2] and results reported in per cent. of color insoluble in water.

The following modification of the paraldehyde test was employed: To 5 cc. of the whiskey in a test-tube add 10 cc. of paraldehyde, and shake vigorously; then add absolute alcohol, a few drops at a time, shaking after each addition until the mixture becomes clear, and allow to stand for about ten minutes. A marked turbidity is shown in samples which contain caramel coloring-matter. This turbidity is best observed by holding the test-tube before and somewhat below a source of light. None of the samples of this series showed any turbidity by this test, while whiskey containing a very small amount of caramel will give a marked turbidity, showing this to be a reliable positive test for caramel.

The samples were also tested by the Marsh method for caramel color, which is as follows: To 5 cc. of the whiskey add 10 cc. of the amyl alcohol reagent, as prepared below. Shake vigorously for a few minutes, and allow to settle. With pure whiskey, the lower layer will be perfectly colorless, while if caramel coloring is present, the lower layer will be colored, depending on the amount of caramel present. The reagent is prepared as follows: To 100 cc. of amyl alcohol add 3 cc. of sirupy phosphoric acid and 3 cc. of water. Shake to form an emulsion before using. The results obtained on the pure whiskies with this method were very satisfactory, the lower layer being water-white, while with whiskey colored with caramel, the color is concentrated in the lower layer, so that very slight additions of caramel to whiskey can be detected.

[1] This Journal, 22, 810–813 (1900).

[2] Proc. Assoc. Official Agr. Chemists, Bulletin 99, U. S. Dept. Agr., Bureau of Chemistry, p. 61.

The amount of color in the two layers also gives a very satisfactory indication of the amount of color due to the whiskey, and the amount of color which has been added.

Statement of Results.

The results of analysis are reported, first, in grams per 100 liters of 100 proof alcohol, and second, in grams per 100 liters calculated to the original volume of the whiskey. This second statement of results was made to show how much the increase taking place in the various constituents as the spirits aged was due to the actual increase of these substances in the barrel, and how much was due to the large decrease in volume which takes place at the same time.

For example, the solid matter in solution in whiskey increases each year to a very marked degree, but when we consider the fact that the volume of the spirit in the barrel has diminished about half during the eight-year period of storage, it is seen that a very large amount of the increase in solids is due to this loss in volume, so that the portion of the table where the results are calculated back to the original volume shows the actual increase of each substance in the barrel, while the first portion of the table shows the changes as they would appear in the whiskey when diluted to 100 proof.

Unfortunately, the data showing the change in volume taking place each year was not available in most cases, only the volume of the spirits as it was stored and the volume left at the end of the seventh and eighth years having been recorded, but from the results found on the few samples for which the data showing the change in volume from year to year were obtained, we feel justified in plotting the curve of the loss in volume from the three points which were determined, and so estimating the yearly changes. All of the results, however, which are based on these calculated yearly changes have been starred in the table.

The loss of the spirits in volume is not due strictly to evaporation (since it must be remembered that the barrels in which these spirits are stored are made as tight as possible to prevent any leakage), but to the passage of the spirits through the pores of the wood. The barrel acts in many ways like the porous membrane of an osmotic cell and has a very decided selective action on the materials passing through it, as is shown by the large percentage increase by reason of concentration of the ethyl alcohol taking place during storage.

The results indicate that water passes through the wood with much greater rapidity than alcohol under the usual conditions in this country.

The results would also indicate, as shown by chart No. III., that the higher alcohols are completely held back. The same selective action

is shown with the acids, esters, aldehydes and furfural. Apparently, these substances are left in the barrel by the selective action of the wooden membrane. It is evident that the chemical changes taking place in the spirit in the formation of acids, esters, etc., are dependent on the storage of the spirit in the porous receptacle, as none of these changes occur when spirit is placed in glass, tin, or even barrels, the inside of which has been covered with paraffin or glue. It is also evident that the condition of the outside of the barrel as to temperature, moisture, etc., will have a decided effect on the rate of osmosis.

Explanation of Terms Used.

The definitions of the terms "Rye" and "Bourbon whiskey" are those given in the circular issued by the Committee on Food Standards of the Association of Official Agricultural Chemists.

"Rye whiskey is whiskey in the manufacture of which rye is the principal cereal used, and Bourbon whiskey is whiskey in which Indian corn is the principal cereal used."

By sweet mash whiskey is meant whiskey in which yeast is used in the fermentation of the mash, and by sour mash whiskey is meant whiskey produced from a mash, the fermentation of which was started by the use of spent beer or slop and barm from tubs previously set and fermented.

The sweet mash fermentation requires much less time for completion, and produces as a rule, a higher percentage of alcohol.

By the term "charred package" is meant a barrel, the staves of which have been charred on the inside more or less deeply by the action of fire. The charring of barrels in which whiskey is to be stored is an almost universal practice in this country.

In order to compare the effects of storage in charred and uncharred packages, two samples of whiskey, Nos. 2625 and 2637, were placed in uncharred packages.

"Proof" is the term used to denote the alcoholic strength of a liquor, and 100 proof is equivalent to 50 per cent by volume of alcohol.

Description of Samples.

Following are the descriptions of the various samples, giving the kind of whiskey, conditions under which it was stored, composition of the mash used, type of still, with amount and kind of rectification, and yield per bushel of grain, taken from the survey of the distillery, as made by the Bureau of Internal Revenue, together with a discussion of the effect of these varying conditions as shown by analytical results:

Whiskey Aged in Charred Packages.

No. 2598 (See Table I): Sweet mash, rye whiskey, entered into warehouse January 6, 1898, in a new, charred, oak barrel; warehouse, dry and above ground; average

temperature, 80° to 85° F. Composition of the mash: malt, 1,064 pounds; and rye, 8,456 pounds. Distilled from copper still, capacity 1,125 gallons; redistilled in a second still of the same capacity. The spirit is run directly from the still to the cistern-room without any form of rectification. Yield per bushel of grain, 4 gallons of proof spirits. The results show the effect of aging in a heated warehouse, there being a large loss in volume, increase in proof and a great amount of acids and esters formed. The product shows a very high flavor.

No. 2599 (See Table I): Sweet mash, rye whiskey, entered into bonded warehouse January 1, 1898, in a new, charred, oak barrel; warehouse, dry and above ground, package was on the fourth floor; average temperature, 85° F. Composition of the mash: malt, 3,696 pounds; rye, 15,008 pounds. Distilled in three-chambered still, with a doubler, all of copper. The spirit is taken directly from the still to the cistern-room without rectification. Yield, 4 gallons of proof spirits to the bushel of grain. This package shows a very great loss of volume on storage, 58 per cent. in six years, and 61 per cent. in seven years, when the package was taken from storage and sold. The proof also increased to an extraordinary degree, changing from 102 at the beginning to 141 at the end of seven years. These changes are greatly hastened by the high temperature of the warehouse, 85° F. the year round. The matured product shows a very fine flavor and taste.

No. 2600 (see Table I): Sweet mash, rye whiskey, entered into warehouse January 1, 1898, in a new, charred, white oak barrel, free of sap; warehouse, dry and above ground; average temperature in winter is 77°, in summer 85° F. Composition of the mash: 997 pounds of malt; 14,041 pounds of rye. Distilled in a large wooden still of 10,000 gallons capacity, with a copper doubler of 2,000 gallons capacity. The spirit goes directly from the doubler to the cistern-room, without any form of rectification. Yield per bushel of grain, 4 gallons of proof spirit. This represents the old style whiskey distilled in the large wooden still.

No. 2601 (see Table II): Sweet mash, rye whiskey, entered into bonded warehouse January 3, 1898, in a new, charred, white oak barrel; warehouse, dry and above ground, with an average temperature in the winter of 80°, in the summer of 90°. Composition of the mash: malt, 2,844 pounds; rye, 14,032 pounds; molasses, 30 gallons. Distilled from a large three-chambered copper beer still, heated by direct steam; capacity, 5,412 gallons, with a small copper still heated with a steam coil, having a capacity of 1,200 gallons, which is used as a doubler. The spirit is taken directly from the still to the cistern-room without rectification. Yield, 4 gallons of proof spirit per bushel of grain. This package shows a large loss in volume and a high temperature in warehouse, 80° in winter and 90° in the summer. This is also the only sample in which molasses or any other form of sugar has been added to the mash.

No. 2602 (see Table II): Sweet mash, rye whiskey, entered in warehouse January 1, 1898, in a new, charred, white oak barrel; warehouse, brick, steam-heated, dry and above ground; average temperature during the first year 85°; afterwards, average temperature 70° Composition of the mash: 3,625 pounds of barley malt; 24,375 pounds Michigan rye. Distilled in a three-chambered copper still, capacity 7,534 gallons, and a copper doubler, capacity 1,000 gallons. The spirits are run from doubler to condenser and then direct to cistern-room, with no other form of rectification. Yield, 4 gallons of proof spirits per bushel of grain.

No. 2603 (see Table II): Sweet mash, rye whiskey, entered into warehouse January 1, 1898, in a new, charred, oak barrel; warehouse, brick, dry, and above ground, with an average temperature of 82°. Composition of the mash: malt, 2,520 pounds; 12,600 pounds rye. Distilled in a large wooden still, capacity 3,554 gallons, heated

by live steam, with a copper doubler, 661 gallons capacity. High wines are diluted to 80° proof, and redistilled in a copper still of 1,050 gallons capacity, heated with a steam coil. Spirit from high wine still, goes directly to the cistern-room without receiving any treatment. Yield per bushel of grain, 4.30 gallons of proof spirit.

No. 2604 (see Table III): Sweet mash, rye whiskey, entered into bonded warehouse January 1, 1898, in a new, fully charred, white oak barrel; warehouse, dry and above ground; average temperature, 80°. Composition of the mash: malt, 6,552 pounds; rye, 22,848 pounds. Distilled in a three-chambered copper beer still, which is charged at intervals. The low wines are redistilled in a copper doubling still, capacity 1,389 gallons. The spirit is run directly from the still to the cistern-room without any form of rectification. Yield, 4 gallons of proof spirit to the bushel of grain.

No. 2605 (see Table III): Sweet mash, rye whiskey, entered into bonded warehouse January 1, 1898, in a new, charred, white oak barrel; warehouse, brick, dry and above ground; average temperature, 70°. Composition of the mash: malt, 2,072 pounds; rye, 12,040 pounds. Distilled in two wooden stills, one of a capacity of 3,827 gallons, the other of 2,625 gallons. Yield, 4 gallons of proof spirits to one bushel of grain. This is an old style "pot still" whiskey, distilled in two large wooden stills, and shows by the amount of fusel oil present that the spirits are not rectified to so great an extent as occurs with the other styles of stills in use.

No. 2606 (see Table III): Sweet mash, rye whiskey, entered into warehouse January 1, 1898, in a charred, white oak barrel; warehouse, brick, dry and above ground; average temperature, 75°. Composition of the mash: malt, 1,680 pounds; rye, 9,520 pounds. Distilled in a large wooden still, capacity 9,695 gallons, with a doubler, capacity 6,060 gallons. The spirit is taken directly from the doubler to the cistern-room without rectification. Yield per bushel of grain, 4 gallons of proof spirit.

No. 2607 (see Table IV): Sweet mash, rye whiskey, entered into warehouse January 3, 1898, in a new, charred, oak barrel; warehouse, brick, dry and above ground; average temperature, 75°. Composition of the mash: malt, 1,260 pounds; rye, 7,140 pounds. Distilled from two wooden pot stills, one with a capacity of 2,158 gallons and one with a capacity of 1,754 gallons, and a copper doubler. The spirit runs directly from the still to the cistern-room, no leach tubes or rectifiers being used in the process. The yield is 4 gallons to the bushel of grain.

No. 2610 (see Table IV): Sweet mash, rye whiskey, entered into warehouse January 1, 1898, in a new, charred, white oak barrel; warehouse, brick, dry and above ground, temperature varying between 60° and 75°. Composition of the mash: malt, 6,720 pounds; rye, 38,080 pounds. Distilled from a copper still, capacity 1,900 gallons; low wine still, capacity 1,500 gallons, with a doubler. The spirit from the stills is run directly to the cistern-room without treatment. Yield per bushel of grain, 4 gallons of proof spirit.

No. 2611 (see Table IV): Sweet mash whiskey in which corn has been used in excess, entered into bonded warehouse January 1, 1898, in a new, charred package, third floor of warehouse; average temperature, winter 40°, summer 70°. Composition of the mash: malt, 5,376 pounds; rye, 31,360 pounds; corn, 41,664 pounds. Two large wooden stills were used. The spirit from the still is doubled in copper doublers, but does not run through charcoal leach tubes going directly from still to cistern-room. Yield, 4 gallons to bushel.

No. 2612 (see Table V): Sweet mash, Bourbon whiskey, entered into bonded warehouse January 1, 1898, in a new, heavily charred, oak barrel; warehouse, dry and above ground; average temperature in the winter is 45°, and in the summer 80°. Composition of the mash: malt, 8,960 pounds; rye, 1,792 pounds; corn, 78,848

pounds. Distilled in a continuous, copper still with a column and doubler, receiving no rectification after leaving the still. Yield, 4.5 gallons of proof spirits per bushel of grain. This sample is evidently very highly rectified in the process of distillation. As shown by the analysis, it contains only a trace of fusel oil and suffered very small loss of volume in aging, perhaps due to being stored in an unheated warehouse. The sample was practically cologne spirits aged in a charred package. The taste of the aged whiskey was very little different from that of new spirits, although the odor was much like that of whiskies stored in wood. Even the eight-year old sample had the taste of spirits, differing in a marked degree in taste from the products distilled in wooden stills in which there was little rectification.

No. 2613 (see Table V): Sour mash, rye whiskey, entered into bonded warehouse January 1, 1898, in a new, charred, oak barrel; warehouse, dry and above ground; average temperature, 70°. Composition of the mash: malt, 2,576 pounds; rye, 29,344 pounds. Distilled in a three-chambered still with a doubler, capacity of the still 6,665 gallons, capacity of the doubler 1,770 gallons. The spirit from the doubler is passed through a charcoal filter before being taken to the cistern-room. Yield, 4.5 gallons to one bushel of grain. This was the only sample of rye whiskey made by the sour mash process, and the only one which was rectified by passing through charcoal filters.

No. 2614 (see Table V): Sweet mash, rye whiskey, entered into bonded warehouse January 15, 1898, in a new, charred, white oak barrel; warehouse, new, dry and above ground; average temperature, 62°. Composition of the mash: rye, 5,950 pounds; malt, 1,050 pounds. Distilled in a large wooden still, capacity 7,766 gallons, with a copper doubling still of 1,065 gallons capacity. The spirits are run direct from the still to the cistern-room without rectification. Yield, 4 gallons of proof spirit to one bushel of grain. This sample shows to a remarkable degree the fact that spirit kept in bottles does not undergo any change. The new spirit having been kept over eight years in bottles was alkaline to phenolphthalein, due doubtless to the water used in diluting the spirit to proof, as compared with the same spirit which had been eight years in wood, which contained 91.9 grams of acid per 100 liters. This shows that the chemical action taking place is largely brought about by the wood and char in the barrel, which act as catalyzing agents.

No. 2623 (see Table VI): Sweet mash, rye whiskey, entered into warehouse January 28, 1898, in a new, charred, white oak barrel; warehouse, brick, dry and above ground; average temperature in winter 65°, in summer 70°. Composition of the mash: rye and barley malt. Distilled in a large three-chambered wooden still, capacity 15,177 gallons, with a copper doubler of 1,116 gallons capacity; redistilled, or run through a copper still before going to the cistern-room. Yield per bushel of grain, 4.5 gallons of proof spirit. Odor and flavor very good in matured goods; body, very light.

No. 2608 (see Table VII): Sour mash, Bourbon whiskey, entered into bonded warehouse January 1, 1898, in a new, charred, white oak barrel; warehouse, dry and above ground; average temperature, 70°. Composition of the mash: malt, 2,240 pounds; rye, 1,400 pounds; corn, 16,500 pounds. Distilled in two copper stills, capacity 2,303 gallons and 2,315 gallons, with two doublers of 1,089 gallons capacity each. Yield, 4 gallons to the bushel of grain.

No. 2609 (see Table VII): Sour mash, Bourbon whiskey, entered into warehouse January 1, 1898, in a new, charred, white oak barrel; warehouse, new, brick, dry and above ground; average temperature in winter 36°, in summer 80°. Composition of the mash: malt, 2,800 pounds; rye, 4,144 pounds; corn, 21,056 pounds.

Distilled in a pot still of 2,000 gallons capacity, with a doubler of 1,000 gallons capacity, both of copper. The spirit is taken directly from the doubler to the cistern-room without any form of rectification. Yield, 4.5 gallons of proof spirit to the bushel of grain. This sample shows a comparatively small loss of volume during the eight years' storage, due to the fact that the warehouse is unheated.

No. 2635 (see Table VII): Sour mash, Bourbon whiskey, entered into bonded warehouse February 7, 1898, in a well-seasoned, charred, white oak barrel, stored on the third floor of a dry, brick warehouse; average temperature, 70° to 80°. The mash is distilled from double pot stills, each of 2,000 gallons capacity, and with a doubler of 900 gallons capacity. The spirit is taken directly from the stills to the cistern-room without passing through any form of rectification. Yield per bushel of grain, 3.75 gallons of proof spirit. Composition of the mash: rye, 2,688 pounds; malt, 4,144 pounds; corn, 30,800 pounds. The low fusel oil indicates that in the doubling of the whiskey a great deal of rectification has taken place. Distilled with wood fire under doubler.

No. 2636 (see Table VIII): Sweet mash, Bourbon whiskey, entered into bonded warehouse February 11, 1898, in a new, charred, oak barrel; warehouse, dry and above ground; the water used for reducing proof is distilled; average temperature in the summer 85°, in the winter 70°. Composition of the mash: malt, 1,288 pounds; rye, 1,400 pounds; corn, 9,744 pounds. Distilled in a chambered still, capacity 4,500 gallons. The spirit runs directly to the cistern-room, no leach tubes or rectifiers being used. Yield, 4.5 gallons to the bushel of grain.

No. 2637 (see Table VIII): Sweet mash, Bourbon whiskey, entered into bonded warehouse February 11, 1898, in a new, charred, white oak barrel; warehouse, brick, dry and above ground; average temperature in the summer 80°, in the winter 48°. Composition of the mash: malt, 6,496 pounds; rye, 8,288 pounds; corn, 27,776 pounds. Distilled in a pot still of 3,525 gallons capacity, with a doubler of 1,395 gallons capacity. The spirit runs directly from the still to the cistern-room without rectification. Yield, 4.5 gallons of proof spirit to the bushel of grain.

No. 2639 (see Table VIII): Sour mash, Bourbon whiskey, entered into bonded warehouse February 8, 1898, in a new, charred, white oak barrel; warehouse, brick, dry and above ground; average temperature in summer 60°–65°, in winter 55°–60°. Composition of the mash: malt, 4,704 pounds; rye, 9,408 pounds; corn, 32,704 pounds. Distilled with a pot still, capacity 4,526 gallons, and a doubler, capacity 1,600 gallons. Yield, 4 gallons of proof spirit per bushel of grain. This sample shows the effect of the temperature of the warehouse in loss of spirits in storage, also the small increase in proof as compared with the samples that show high losses of volume.

No. 2684 (see Table IX): Sour mash, Bourbon whiskey, entered into bonded warehouse March 31, 1898, in a new, charred, oak barrel; warehouse, frame, dry and above ground; average temperature in summer 70°, in winter 40°. Composition of the mash: malt, 2,800 pounds; rye, 1,680 pounds; corn, 15,680 pounds. Distilled in a large pot still, capacity 8,000 gallons, with a doubler of 1,400 gallons. The spirit is taken directly from the doubler to the cistern-room without rectification of any kind. Yield, 4 gallons of proof spirit to one bushel of grain.

No. 2683 (see Table IX): Sour mash, corn whiskey, entered into bonded warehouse April 9, 1898, in a new, charred, oak barrel; warehouse, brick and heated by steam. Average temperature in summer 75°, in winter 40°. Composition of the mash: malt, 1,176 pounds; rye, 840 pounds; corn, 9,184 pounds. Distilled with a three-chambered still to 60° proof, then doubled in a pot still heated by fire. The

spirits from the doubler are run through charcoal leach tubes before going to the cistern-room. Yield, 4.25 gallons per bushel of grain.

No. 2644 (see Table IX): Sour mash, Bourbon whiskey, entered into bonded warehouse January 20, 1898, in a new, charred, white oak barrel; warehouse, iron-clad, dry and above ground, not artificially heated. Composition of the mash: malt, 616 pounds; rye, 924 pounds; corn, 7,952 pounds. Distilled in a pot still with a capacity of 3,374 gallons, and with a doubler, capacity of 1,500 gallons. The spirt is run directly into the cistern-room, without any form of rectification. Yield, 4.5 gallons to one bushel of grain. This whiskey shows a slight loss of volume, as compared with the other whiskies, and at the same time the changes taking place in the package have been much less active, as shown by the slight change in proof and relatively small amounts of color, solids, acids, and esters. This emphasizes the fact that reactions taking place in the aging of the product are due largely to the temperature and the rate of osmosis, or the passage of the spirit through the wood.

No. 2685 (see Table X): Sour mash, Bourbon whiskey, entered into bonded warehouse April 9, 1898, in a new heavily charred white oak barrel; warehouse, dry and above ground. Average temperature in the summer is 80°, in the winter 45°. Composition of the mash: malt, 1,960 pounds; rye, 7,840 pounds; corn, 5,600 pounds. Entered as a Bourbon whiskey, but contains rye in excess, as shown by the composition of the mash. Distilled in a continuous, copper, beer still, the low wines from which are doubled in a copper doubler and are not rectified or refined in any way after leaving the doubler, and before reaching the cistern-room. Yield, 3.5 gallons of proof spirits per bushel of grain.

No. 2686 (see Table X): Sour mash, Bourbon whiskey, entered in bonded warehouse April 12, 1898, in a new, heavily charred, oak barrel; warehouse, dry and heated by steam. Average temperature in summer 70°, in winter 65°. Composition of the mash: malt, 6,272 pounds; rye, 5,432 pounds; corn, 36,512 pounds. Distilled in a beer still 23 feet high, with a doubler, the column being about the same height as the beer still. Capacity of the still 3,480 gallons; capacity of the doublers 1,440 gallons. The spirit is taken directly from the doubler to the cistern-room without any form of rectification.

No. 2689 (see Table X): Sour mash, corn whiskey, entered into bonded warehouse April 4, 1898, in a new, charred, oak barrel; warehouse, dry and above ground; samples on the top shelf; average temperature in summer 72°, in winter 42°. Composition of the mash: malt, 336 pounds; rye, 224 pounds; corn, 2,968 pounds. Distilled in a copper still with a column. The low wines are redistilled in a doubler which is practically a large pot-still. The beer still has a capacity of 1,200 gallons and the doubler of 800 gallons. The spirit from the doubler is leached through tall, narrow vats, into which powdered charcoal has been packed. The whiskey slowly percolates through this charcoal, taking several days to reach the cistern-room. The charcoal used in this leaching is made by burning sugar-maple wood in the open air. The yield per bushel of grain is 3.75 gallons of proof spirits. The very low content of fusel oil shows that considerable rectification has taken place. The high ash of the product indicates that in leaching through the charcoal large quantities of mineral matter are dissolved. The high amount of solids is due largely to the ash. The flavor is good and also the aroma.

No. 2689 A (see Table XI): Sour mash, corn whiskey, entered into bonded warehouse April 9, 1898, in a new, charred, oak barrel. Composition of the mash: malt, 672 pounds; rye, 728 pounds; corn, 5,824 pounds. Distilled in a chambered still with a large doubler, 4,000 gallons capacity. The spirits from the doubler is run through leach tubes, filled with charcoal. Yield, 4.5 gallons per bushel of grain.

Following are the tables of analyses I to XII:

TABLE III.

Time in wood.	Wine gallons in barrel.	Proof.	Color calculated to 100 proof.	Grams per 100 liters of 100 proof spirit. Solids.	Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Grams per 100 liters calculated to the original volume. Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Color removed by ether.	Color insoluble in water.	Caramel color. Paraldehyde test.	Marsh test.
Lab. No. 2604.							**Rye Whiskey, Sweet Mash.**											
New	45.09	100.0	0.0	16.0	17.2	18.5	2.2	1.5	128.0	7.2	18.5	2.2	1.5	128.0	0.0	....	...	...
1 year	....	102.0	11.2	150.0	47.6	36.2	3.6	1.7	132.0	45.1*	34.8*	6.7*	1.7*	126.8*	15.2	50.0	Neg	Neg
2 years	....	106.0	14.8	171.0	47.5	53.9	9.4	2.5	154.7	44.5*	50.4*	8.8*	2.3*	144.5*	39.8	....	"	"
3 "	....	108.0	16.3	185.0	58.9	66.0	11.0	2.6	168.5	52.4*	58.8*	9.9*	2.3*	150.0*	41.9	66.0	"	"
4 "	....	111.0	16.2	197.0	59.6	64.2	13.5	3.1	180.0	49.9*	54.9*	11.5*	2.6*	154.0*	36.0	....	"	"
5 "	....	111.0	18.8	214.0	66.2	67.2	15.0	3.4	156.8	52.4*	53.1*	12.0*	2.7*	123.5*	39.0	70.0	"	"
6 "	....	114.0	19.3	221.0	66.9	72.5	15.8	3.5	177.2	49.8*	54.1*	11.7*	2.6*	132.0*	41.0	....	"	"
7 "	26.87	113.0	19.4	231.0	70.4	68.5	16.0	3.5	187.6	47.4	46.1	11.3	2.4	126.3	41.0	70.0	"	"
8 "	25.33	114.0	19.3	241.0	73.7	73.3	16.6	4.0	189.4	47.1	46.9	10.6	2.6	121.3	43.0	....	"	"
Lab. No. 2605.							**Rye Whiskey, Sweet Mash.**											
New	45.20	100.0	0.0	6.0	1.2	....	....	...	....	1.2	....	...	....	....	....	....	...	...
1 year	....	103.0	8.2	112.0	37.9	33.2	7.76	3.3	194.0	36.4*	31.9*	7.45*	3.16*	186.4*	14.7	21.0	Neg	Neg
2 years	....	106.0	10.3	132.0	48.6	41.5	....	...	214.0	44.7*	38.1*	....	....	196.8*	40.2	....	"	...
3 "	....	109.0	11.4	149.0	61.6	50.0	12.4	3.7	202.0	54.0*	44.0*	10.9*	3.2*	176.9*	40.0	40.0	"	Neg
4 "	....	115.0	13.0	156.0	68.8	66.6	12.5	4.8	203.5	58.6*	56.6*	10.6*	4.0*	173.2*	35.0	....	"	"
5 "	....	118.0	14.4	184.0	71.1	75.3	12.7	5.1	254.2	56.7*	59.6*	10.1*	4.0*	202.0*	33.0	57.0	"	"
6 "	....	124.4	17.2	226.0	79.2	86.9	12.8	5.2	245.3	58.6*	65.9*	9.7*	4.0*	185.4*	38.0	....	"	...
7 "	24.68	127.0	18.9	243.0	73.7	85.4	12.6	4.8	264.5	51.1	59.3	8.8	3.3	183.4	36.0	66.0	"	Neg
8 "	22.28	132.0	20.8	262.0	76.3	95.0	13.6	5.1	280.3	49.7	61.8	8.8	3.3	182.4	44.0	71.0	"	"
Lab. No. 2606.							**Rye Whiskey, Sweet Mash.**											
New	46.76	100.0	0.0	7.0	3.6	14.1	4.8	1.9	86.0	3.6	14.1	4.8	1.9	86.0	0.0	....	....	....
1 year	....	101.0	7.9	106.0	59.4	27.9	5.4	2.2	93.0	56.0*	26.3*	5.0*	2.15*	87.8*	12.5	32.0	Neg	Neg
2 years	....	103.0	12.3	153.0	75.6	75.1	5.4	1.9	85.0	68.6*	68.1*	4.9*	1.8*	77.4*	40.0	....	"	"
3 "	....	107.0	14.2	174.0	81.8	79.8	6.5	2.3	101.0	71.8*	70.0*	5.7*	2.0*	89.4*	40.0	52.0	"	"
4 "	....	110.0	15.0	192.0	82.9	83.2	6.4	2.7	101.0	69.8*	70.0*	5.4*	2.3*	85.7*	40.0	....	"	"
5 "	....	114.0	17.9	196.0	92.6	83.4	6.6	2.8	115.0	74.1*	66.7*	5.3*	2.3*	92.6*	33.0	63.0	"	...
6 "	....	119.0	18.5	228.0	96.8	66.4	7.3	2.9	124.0	74.3*	50.9*	5.7*	2.3*	95.4*	38.0	....	"	Neg
7 "	27.27	120.0	20.4	255.0	100.0	99.7	7.5	3.0	127.0	70.0	69.8	5.3	2.1	88.6	41.0	69.0	"	"
8 "	25.25	124.0	22.6	285.0	104.6	110.7	7.9	3.1	127.0	69.9	74.1	5.2	2.0	85.3	44.0	71.0	"	"

TABLE IV.

Time in wood.	Wine gallons in barrel.	Proof.	Color calculated to 100 proof.	Grams per 100 liters of 100 proof spirits. Solids.	Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Grams per 100 liters calculated to the original volume. Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Color removed by ether.	Color insoluble in water.	Caramel color. Paraldehyde test.	Marsh test.
Lab. No. 2607.								RYE WHISKEY, SWEET MASH.										
New	45.14	100.0	0.0	5.0	5.9	11.2	3.9	0.9	78.0	6.0	11.4	4.0	1.0	79.0	0.0	....	...	...
1 year	....	103.0	13.8	171.0	....	....	....	...	....	....	....	...	...	....	16.0	....	?	...
2 years	....	106.0	16.7	199.0	73.5	68.0	10.3	2.4	....	67.1*	61.9*	9.4*	2.1*	....	40.0	....	?	Neg
3 "	....	109.0	18.3	224.0	80.7	78.2	11.4	2.3	79.0	69.5*	67.4*	9.8*	1.9*	67.9*	40.0	66.0	Neg	...
4 "	....	111.0	18.9	238.0	83.8	87.2	13.4	2.7	95.5	66.9*	69.7*	10.7*	2.1*	76.3*	36.0	....	"	Neg
5 "	....	112.0	19.2	251.0	84.8	91.2	....	2.8	97.3	61.9*	66.6*	9.64*	2.1*	71.0*	37.0	69.0	"	"
6 "	....	115.0	20.4	249.0	88.6	91.8	13.4	3.5	80.0	59.5*	61.6*	9.0*	2.3*	53.6*	41.0	....	"	"
7 "	23.22	116.0	20.7	260.0	94.0	....	....	...	112.0	56.0	....	...	...	66.8	42.0	73.0	"	...
8 "	21.79	120.0	20.4	260.0	96.7	100.0	13.7	3.8	111.0	56.0	57.8	7.9	2.1	64.7	43.0	71.0	"	...
Lab. No. 2610.								RYE WHISKEY, SWEET MASH.										
New	47.1	102.0	0.0	6.0	6.0	18.1	2.9	0.5	61.8	6.0	18.5	3.0	0.500	63.0	0.0	....	...	...
1 year	....	102.0	6.6	92.0	55.3	40.8	4.71	0.58	66.6	52.7*	38.9*	4.4*	0.56*	63.5*	11.1	23.0	Neg	Neg
2 years	....	104.0	8.6	121.0	61.7	47.8	8.6	1.6	88.4	55.8*	43.2*	7.83*	1.48*	80.0*	40.3	....	"	"
3 "	....	107.0	11.9	154.0	67.3	60.5	9.9	3.0	85.0	58.0*	52.1*	8.54*	2.58*	73.3*	41.6	57.0	"	"
4 "	....	111.0	12.1	156.0	71.7	72.1	10.2	2.2	83.8	59.1*	59.5*	8.47*	1.78*	69.1*	44.0	....	"	"
5 "	....	112.0	15.1	181.0	78.5	76.1	11.8	2.3	78.5	59.8*	58.0*	8.98*	1.77*	59.8*	44.0	64.0	"	"
6 "	....	114.0	15.3	193.0	84.7	83.2	12.6	2.5	....	59.6*	58.6*	8.88*	1.73*	....	44.0	....	"	"
7 "	26.06	120.0	15.4	195.0	86.0	88.0	12.6	2.6	99.2	59.0	58.4	8.3	1.77	65.8	47.0	66.0	"	"
8 "	23.13	124.7	15.2	224.0	93.1	93.3	12.8	2.6	113.9	57.0	57.1	7.80	1.6	69.6	43.0	67.0	"	"
Lab. No. 2611.								BOURBON WHISKEY, SWEET MASH.										
New	45.47	100.7	3.10	33.0	2.4	11.4	3.6	trace	107.2	24.0	11.4	3.6	trace	108.0	12.7	....	...	...
1 year	....	101.5	8.87	122.0	45.5	20.8	4.33	7.9	135.0	40.6*	18.5*	3.8*	7.0*	120.2*	13.9	28.0	Neg	Neg
2 years	....	103.0	11.6	160.0	57.1	34.2	12.0	9.1	136.9	50.5*	50.3*	10.66*	8.08*	121.0*	41.4	....	"	"
3 "	....	105.0	13.8	184.0	59.1	63.7	22.1	9.5	134.3	50.3*	56.1*	19 4*	8.3*	118.3*	40.0	62.0	"	"
4 "	....	108.0	14.3	196.0	70.0	72.1	22.2	9.63	109.2	54.7*	56.4*	17.4*	7.5*	85.6*	38.0	....	"	"
5 "	....	112.5	16.1	217.0	72.5	74.3	23.1	9.60	129.8	56.3*	57.7*	17.9*	7.45*	89.7*	44.0	61.0	"	"
6 "	....	116.0	16.4	234.0	77.6	82.7	23.3	9.48	151.7	57.6*	61.4*	17.3*	7.04*	112.6*	43.0	....	"	"
7 "	26.36	120.0	17.9	255.0	82.5	80.7	26.7	8.33	148.3	57.4	56.1	18.6	5.80	103.2	45.0	67.0	"	"
8 "	24.02	124.1	18.5	278.0	88.1	93.6	28.8	10.0	170.0	57.7	61.3	19.0	6.5	99.6	46.0	72.0	"	...

TABLE V.

Time in wood.	Wine gallons in barrel.	Proof.	Color calculated to 100 proof.	Grams per 100 liters of 100 proof spirit. Solids.	Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Grams per 100 liters calculated to original volume. Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Color removed by ether.	Color insoluble in water.	Caramel color. Paraldehyde test.	Marsh test.
Lab. No. 2612. BOURBON WHISKEY, SWEET MASH.																		
New	47.4	100.0	0.0	4.0	3.0	9.7	1.8	trace	3.0	3.0	9.7	1.8	trace	3.0	0.0	....	...	...
1 year	43.91	102.0	9.8	95.0	43.5	10.4	2.7	1.4	7.84	41.1	9.8	2.6	1.29	7.4	10.0	54.0	...	...
2 years	....	103.0	9.9	133.0	48.5	40.8	8.5	1.6	5.8	44.3*	37.6*	7.8*	1.4*	5.3*	40.0	....	Neg	Neg
3 "	40.50	103.0	12.1	150.0	51.8	41.4	12.0	1.6	7.9	45.5	36.4	10.5	1.3	6.8	39.1	64.0	"	"
4 "	38.15	105.0	12.4	160.0	56.0	45.2	12.0	1.5	9.5	47.2	38.2	10.1	1.3	8.0	43.0	....	"	"
5 "	36.68	107.0	14.5	181.0	59.0	46.8	12.1	1.6	11.2	49.2	38.7	10.0	1.3	9.2	42.0	60.0	"	"
6 "	35.15	108.0	15.3	196.0	63.3	53.0	12.2	1.7	6.4	50.7	42.4	9.8	1.3	5.1	41.0	....	"	"
7 "	33.75	109.0	16.1	207.0	69.9	57.6	12.9	1.6	17.4	54.2	44.9	9.9	1.2	13.5	42.0	64.0	"	"
8 "	32.48	110.4	16.3	217.0	71.7	58.1	13.4	1.6	19.0	54.2	44.0	10.1	1.2	14.3	42.0	58.0	"	"
Lab. No. 2613. RYE WHISKEY, SOUR MASH.																		
New	46.57	100.6	0.0	11.0	6.0	6.2	trace	....	101.5	6.0	6.2	trace	....	102.0	0.0	....	...	...
1 year	....	101.0	7.18	93.0	39.8	6.8	5.15	0.39	108.9	38.1*	65.4*	4.93*	0.38*	104.0*	13.8	34.0	Neg	Neg
2 years	....	100.0	8.75	123.0	48.0	52.8	8.0	0.70	135.0	43.0*	47.3*	7.17*	0.627*	121.0*	41.0	....	"	"
3 "	....	104.0	10.1	145.0	55.3	52.5	12.1	0.70	141.4	48.8*	46.2*	10.7*	0.593*	125.0*	38.0	33.0	"	"
4 "	....	106.0	11.3	153.0	57.7	57.7	12.8	0.70	146.2	48.8*	48.8*	10.8*	0.597*	117.0*	38.0	....	"	"
5 "	....	108.0	13.9	170.0	59.4	65.0	....	....	132.4	47.9*	49.9*	....	....	106.7*	36.0	50.0	"	"
6 "	....	110.0	14.1	193.0	67.1	64.0	13.1	0.70	135.5	51.4*	49.0*	10.0*	0.557*	103.0*	36.0	....	"	"
7 "	30.09	113.0	14.6	207.0	65.1	64.6	13.8	0.80	156.0	47.5	47.4	10.0	0.50	113.8	36.0	59.0	"	"
8 "	27.70	114.6	15.7	221.0	73.8	72.2	15.4	0.80	169.3	50.3	49.2	10.4	0.50	106.6	36.0	56.0	"	"
Lab. No. 2614. RYE WHISKEY, SWEET MASH.																		
New	44.9	102.0	0.0	30.0	alk.	6.8	4.39	0.09	43.7	alk.	7.0	4.4	0.100	44.0	0.0	....	...	...
1 year	....	102.0	9.3	144.0	58.8	31.1	5.9	2.39	80.4	46.6*	29.4*	5.6*	2.24*	76.4*	13.2	58.0	Neg	Neg
2 years	....	103.0	13.3	175.0	65.0	54.7	6.9	2.91	83.4	52.4*	48.9*	6.14*	2.6*	74.6*	39.7	....	"	"
3 "	....	105.7	14.2	199.0	71.3	58.1	11.0	2.83	85.1	60.7*	49.5*	8.96*	2.4*	72.3*	41.3	62.0	"	"
4 "	....	108.0	14.8	216.0	78.9	81.5	15.5	2.96	92.6	63.0*	65.1*	12.4*	2.37*	74.0*	35.0	....	"	"
5 "	....	113.0	17.7	250.0	81.8	83.7	16.6	3.5	100.8	62.5*	63.9*	12.7*	2.70*	77.1*	34.0	69.0	"	"
6 "	....	118.0	19.5	284.0	85.4	85.0	16.9	4.6	110.1	61.4*	61.2*	12.2*	3.29*	79.3*	33.0	....	"	"
7 "	24.12	121.0	21.1	296.0	85.3	84.8	16.5	4.13	110.7	55.4	54.8	11.7	2.68	71.9	35.0	72.0	"	"
8 "	21.98	124.2	21.4	310.0	91.9	79.1	17.4	4.0	121.0	55.8	53.4	10.5	2.4	73.4	40.0	71.0	"	"

TABLE VI.

Time in wood.	Wine gallons in barrel.	Proof.	Color calculated to 100 proof.	Grams per 100 liters of 100 proof spirit.						Grams per 100 liters calculated to original volume.					Color removed by ether.	Color insoluble in water.	Caramel color.	
				Solids.	Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.			Paraldehyde test.	Marsh test.
Lab. No. 2623.				RYE WHISKEY, SWEET MASH.														
New	44.49	102.0	....	26.0	3.5	4.3	5.9	...	78.6	3.6	4.4	6.0	....	80.0	0.0	....	...	...
1 year	....	103.0	7.52	107.0	5.8	6.8	7.8	2.0	80.6	5.6*	6.54*	....	1.96*	77.9*	12.9	23.0	Neg	Neg
2 years	....	104.6	9.8	133.0	11.0	31.2	8.0	2.0	82.2	10.0*	28.7*	7.40*	1.76*	75.8*	38.1	....	"	"
3 "	....	107.6	11.6	152.0	16.4	34.3	8.5	2.2	....	14.5*	30.3*	7.56*	1.97*	78.1*	40.0	34.0	"	"
4 "	....	111.0	11.7	157.0	17.3	36.3	9.0	2.1	85.6	14.6*	30.9*	7.64*	1.53*	72.6*	38.0	....	"	"
5 "	....	114.0	11.8	168.0	19.0	37.0	9.2	2.5	86.8	15.2*	29.7*	7.53*	1.97*	69.8*	36.0	....	"	"
6 "	....	117.0	12.4	176.0	24.6	39.1	10.6	2.6	99.2	18.6*	29.5*	8.03*	1.94*	74.9*	40.0	....	"	"
7 "	26.19	122.0	13.1	194.0	24.7	41.8	11.5	3.0	104.1	17.7	30.0	8.25	2.12	74.8	40.0	47.0	"	"
8 "	23.66	126.9	13.8	200.0	31.7	40.9	12.6	2.8	107.1	21.3	27.6	8.5	1.80	72.3	47.0	63.0	"	...

TABLE VII.

Time in wood.	Wine gallons in barrel.	Proof.	Color calculated to 100 proof.	Grams per 100 liters of 100 proof spirit. Solids.	Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Grams per 100 liters calculated to the original volume. Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Color removed by ether.	Color insoluble in water.	Caramel color. Paraldehyde test.	Marsh test.
Lab. No. 2608. BOURBON WHISKEY, SOUR MASH.																		
New	48.79	103.0	...	11.7	29.1	42.7	4.3	0.200	112.0	30.0	44.0	4.40	0.200	116.0	0.0	....	...	...
1 year	....	103.0	7.3	94.0	43.7	44.7	5.43	0.188	124.0	42.5*	43.5*	5.30*	0.188*	120.8*	13.3	50.0	Neg	Neg
2 years	....	104.0	8.9	117.0	55.4	45.9	7.7	0.38	117.3	51.6*	42.7*	7.17*	0.36*	109.3*	48.0	....	"	"
3 "	....	105.0	10.9	132.0	61.7	67.9	12.2	1.1	118.1	54.7*	60.2*	10.8*	1.0*	104.8*	42.1	60.0	"	"
4 "	....	107.0	11.6	142.0	67.2	75.2	13.4	1.2	123.3	57.3*	64.1*	11.4*	1.0*	105.0*	42.0	....	"	"
5 "	....	108.0	12.5	157.0	70.0	79.0	13.7	1.3	144.0	56.3*	63.5*	11.0*	1.0*	116.0*	40 0	65.0	"	"
6 "	....	110.0	14.0	171.0	73.1	79.7	14.1	1.4	141.8	55.8*	60.8*	10.8*	1.0*	108.3*	42.0	....	"	"
7 "	31.43	112.0	13.8	178.0	83.9	81.7	....	1.4	141.0	54.1	59.0	10.3	1.0	101.8	43.0	67.0	"	"
8 "	28.49	115.0	14.7	190.0	82.4	86.4	14.9	1.6	137.4	54.7	57.4	9.9	1.0	91.2	49.0	62.0	"	"
Lab. No. 2609. BOURBON WHISKEY, SOUR MASH.																		
New	47.5	102.0	...	14.0	....	....	....	....	161.8	....	....	....	....	165.0	0.0	...	...	...
1 year	....	102.0	7.1	91.0	43.5	31.1	2.7	0.90	161.8	42.2*	30.2*	2.6*	0.80*	157.1*	13.7	37.0	Neg	Neg
2 years	....	103.0	9.4	123.0	47.8	37.6	7.00	0.88	170.8	44.6*	34.8*	6.5*	0.86*	159.4*	38.8	....	"	"
3 "	....	103.0	11.4	146.0	54.8	47.0	10.5	1.2	177.7	48.5*	41.6*	9.2*	1.3*	157.4*	40.0	45.0	"	"
4 "	....	104.0	12.0	155.0	49.6	50.8	11.2	1.9	183.0	42.0*	43.0*	9.4*	1.6*	179.3*	34.0	....	"	"
5 "	....	107.0	13.1	164.0	60.6	53.9	12.0	2.1	179.0	49.9*	44.4*	9.8*	1.7*	135.5*	34.0	52.0	"	"
6 "	....	109.0	13.8	182.0	65.0	57.7	12.5	2.1	177.1	50.9*	45.3*	9.9*	1.6*	139.0*	40.0	....	"	...
7 "	32.14	110.0	14.5	195.0	69.3	60.8	12.7	2.2	185.5	51.5	44.6	9.5	1.6	138.0	45.0	62.0	"	Neg
8 "	30.89	111.0	14.4	211.0	74.1	66.6	12.3	2.3	199.1	53.4	48.0	8.8	1.6	143.6	45.0	66.0	"	"
Lab. No. 2635. BOURBON WHISKEY, SOUR MASH.																		
New	47.92	102.0	...	17.6	7.0	9.5	2.0	0.6	84.0	7.2	9.7	2.0	0.6	86.0	0.0	....	...	...
1 year	....	101.7	5.9	86.0	34.2	10.4	3.4	....	83.0	33.1*	10.1*	2.5*	....	79.8*	12.5	35.0	Neg	Neg
2 years	....	102.0	6.9	106.0	45.5	42.8	7.8	0.60	94.0	44.4*	41.7*	7.21*	0.541*	85.7*	49.3	....	"	"
3 "	....	104.0	...	154.0	....	52.9	8.8	0.60	96.0	....	47.1*	7.87*	0.514*	85.6*	41.7	57.0	...	...
4 "	....	105.0	8.6	122.0	60.6	46.1	9.5	0.80	95.0	51.8*	39.6*	8.18*	0.654*	81.0*	34.0	....	Neg	Neg
5 "	....	106.0	11.8	143.0	52.1	45.7	9.8	0.80	98.0	41.9*	36.8*	7.90*	0.608*	79.0*	38.0	52.0	...	...
6 "	....	108.5	12.0	148.0	64.1	50.7	10.3	0.90	99.0	46.5*	40.2*	7.84*	0.713*	76.2*	48.0	....	Neg	Neg
7 "	31.88	110.0	11.8	158.0	63.3	52.9	12.6	0.91	115.0	46.3	38.5	8.60	0.665	87.4	48.0	52.0	...	...
8 "	29.89	110.0	12.3	165.0	74.2	59.6	12.0	1.1	114.0	50.9	40.9	8.20	0.700	78.0	50.0	61.0	Neg	Neg

TABLE VIII.

Time in wood.	Wine gallons in barrel.	Proof.	Color calculated to 100 proof.	Grams per 100 liters of 100 proof spirit. Solids.	Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Grams per 100 liters, calculated to the original volume. Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Color removed by ether.	Color insoluble in water.	Caramel color. Paraldehyde test.	Marsh test.
Lab. No. 2636.							BOURBON WHISKEY, SWEET MASH.											
New	45.8	101.0	0.0	4.0	5.9	9.6	7.9	....	122.8	6.0	9.7	8.0	....	123.0	0.0	....	...	...
1 year	....	102.0	7.11	97.0	35.3	24.1	8.6	0.88	135.3	34.3*	23.6*	8.4*	0.86*	131.7*	17.3	21.0	Neg	Neg
2 years	....	102.5	8.78	118.0	46.8	47.2	8.60	1.10	134.6	43.7*	44.1*	8.01*	1.00*	125.6*	38.8	....	"	"
3 "	....	103.0	9.94	142.0	59.4	49.1	9.30	1.10	124.3	53.0*	43.9*	8.32*	0.954*	110.9*	37.5	53.0	"	"
4 "	....	105.0	11.9	152.0	62.8	55.3	9.50	1.10	126.0	54.3*	47.1*	8.23*	0.988*	108.6*	38.0	....	"	"
5 "	....	107.5	13.5	182.0	65.8	57.3	9.70	1.20	....	55.2*	48.0*	8.11*	1.01*	....	43.0	57.0	"	"
6 "	....	109.6	14.1	186.0	73.0	64.2	9.80	1.20	127.2	58.8*	51.8*	7.95*	0.971*	103.1*	45.0	....	"	"
7 "	31.78	112.0	14.7	204.0	77.1	66.2	10.0	1.07	130.4	59.9	51.3	7.77	0.833	101.4	45.0	61.0	"	"
8 "	29.85	112.0	15.6	215.0	79.3	64.5	10.70	1.30	133.9	57.8	47.0	7.20	0.900	97.8	47.0	62.0	"	"
Lab. No. 2637.							BOURBON WHISKEY, SWEET MASH.											
New	47.02	101.0	0.0	9.0	1.19	24.0	0.9	trace	171.3	1.2	24.2	0.9	trace	178.0	0.0	....	...	...
1 year	....	101.5	8.12	116.0	38.4	26.0	7.8	0.79	173.4	37.0*	24.9*	7.5*	0.75*	166.0*	9.1	60.0	Neg	Neg
2 years	....	102.7	9.49	146.0	23.3	33.0	8.2	0.80	178.2	21.3*	30.1*	7.45*	0.709*	162.0*	38.5	....	"	"
3 "	....	103.0	....	185.0	52.4	43.6	10.1	0.90	180.6	44.8*	37.3*	8.64*	0.748*	154.0*	40.0	61.0	"	"
4 "	....	105.0	13.3	170.0	54.1	48.6	9.9	0.90	199.0	44.1*	39.6*	8.07*	0.698*	162.0*	33.0	....	"	"
5 "	....	108.0	14.3	207.0	61.0	57.7	....	0.93	....	47.8*	44.7*	....	0.72*	....	32.0	53.0	"	"
6 "	....	111.0	15.7	220.0	67.0	57.5	12.6	0.90	217.1	49.7*	42.6*	9.35*	0.701*	161.0*	31.0	....	"	"
7 "	28.66	113.0	16.4	245.0	72.2	63.1	12.7	1.0	221.2	49.7	42.9	8.8	0.730	152.0	32.0	59.0	"	"
8 "	27.15	114.0	18.0	255.0	78.9	66.4	13.0	1.1	221.0	51.9	43.7	8.50	0.700	146.0	34.0	67.0	"	"
Lab. No. 2639.							BOURBON WHISKEY, SOUR MASH.											
New	46.63	100.7	0.0	10.0	7.2	15.8	0.99	none	115.1	7.2	15.8	1.0	none	116.0	0.0	....	...	...
1 year	....	101.2	8.64	114.0	44.5	27.9	6.7	1.38	108.7	42.9*	26.9*	6.49*	1.34*	105.0*	11.4	43.0	Neg	Neg
2 years	....	101.8	11.8	136.0	51.3	34.6	7.46	1.47	123.7	47.5*	32.0*	7.10?	1.37*	115.0*	51.1	....	"	"
3 "	....	102.0	12.2	154.0	58.8	52.6	7.8	1.5	137.2	52.1*	46.6*	6.94*	1.30*	121.0*	40.0	50.0	"	"
4 "	....	103.0	13.1	159.0	64.1	53.1	10.1	1.7	118.4	54.3*	44.9*	8.56*	1.40*	100.0*	37.0	....	"	"
5 "	....	104.0	14.4	184.0	64.6	53.2	9.60	1.8	136.5	52.4*	43.2*	7.80*	1.40*	111.0*	40.0	50.0	"	"
6 "	....	105.0	14.7	200.0	69.7	60.4	9.5	1.7	118.1	53.9*	46.7*	7.36*	1.32*	125.0*	40.0	....	"	"
7 "	32.33	107.0	16.3	216.0	74.4	59.8	9.3	1.68	158.9	55.2	44.0	6.93	1.25	118.0	44.0	64.0	"	"
8 "	30.51	113.5	15.9	216.0	74.0	58.1	9.1	1.8	142.7	54.9	43.1	6.80	1.20	106.0	44.0	64.0	"	"

TABLE IX.

Time in wood.	Wine gallons in barrel.	Proof.	Color calculated to 100 proof.	Grams per 100 liters of 100 proof spirit. Solids.	Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Grams per 100 liters, calculated to original volume. Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Color removed by ether.	Color insoluble in water.	Caramel color. Paraldehyde test.	Marsh test.
Lab. No. 2644.							**Bourbon Whiskey, Sour Mash.**											
New	47.94	103.5	0.0	9.00	3.4	11.9	2.3	....	74.4	3.6	12.3	2.4	....	77.0	0.0	....	...	...
1 year	....	102.5	4.63	65.0	26.3	17.2	3.5	0.98	83.9	25.8*	16.8*	3.4*	0.095*	82.3*	10.5	57.0	Neg	Neg
2 years	....	101.0	5.69	85.0	34.4	33.0	9.90	0.800	87.1	31.8*	30.5*	9.14*	0.731*	80.4*	43.5	50.0	"	"
3 "	....	100.0	7.00	99.0	38.4	31.7	11.20	0.800	88.0	33.5*	27.6*	9.76*	0.697*	82.8*	40.0	58.0	"	"
4 "	....	101.0	7.40	101.0	40.4	34.8	12.3	1.00	103.9	33.9*	29.2*	10.3*	0.996*	88.8*	38.0	....	"	"
5 "	....	101.0	8.40	125.0	42.7	35.7	12.7	1.20	105.9	34.0*	28.5*	9.54*	0.946*	84.3*	36.0	56.0	"	"
6 "	....	101.6	9.30	132.0	45 0	36.4	12.6	1.00	108.2	34.1*	27.6*	9.55*	0.746*	82.1*	41.0	....	"	"
7 "	33.75	102.0	10.05	147.0	49.0	37.1	12.7	0.98	106.8	35.4	27.1	9.14	0.703	76.7	39.0	63.0	"	"
8 "	32.73	102.7	10.45	152.0	53.7	37.7	13.6	1.20	106.1	37.6	26.4	9.50	0.800	74.4	37.0	58.0	"	"
Lab. No. 2683.							**Bourbon Whiskey, Sour Mash.**											
New	45.0	103.0	0.0	5.0	16.3	25.6	1.9	none	114.6	16.8	26 4	2.0	none	118.0	0.0	....	...	...
1 year	....	102.0	10.9	88.0	42.3	26.5	7.8	0.59	119.6	40.8*	25.5*	7.52*	0.56*	115.0*	11.1	30.0	Neg	Neg
2 years	....	103.0	8.98	110.0	47.8	47.0	8.10	1.40	122.3	44.8*	43.4*	7.52*	1.25*	112.8*	42.5	63.0	"	"
3 "	....	104.0	9.37	122.0	53.0	48.3	9.20	1.50	121.1	46.6*	42.4*	8.11*	1.35*	106.4*	40.0	63.0	"	"
4 "	....	105.0	9.50	130.0	54.9	49.3	9.5	1.5	133.3	45.9*	41.1*	7.96*	1.27*	111.4*	41.0	....	"	"
5 "	....	107.0	12.1	149.0	54.6	51.8	9.30	1.60	149.5	43.4*	41.2*	7.44*	1.26*	119.0*	42.0	62.0	"	"
6 "	....	108.6	13.4	151.0	63.0	55.0	9.90	1.70	149.3	47.5*	41.5*	7.49*	1.25*	112.4*	43.0	....	"	"
7 "	28.89	112.0	13.8	171.0	62.1	62.8	9.8	1.6	148.2	44.7	45.2	7.06	1.16	106.6	43.0	64.0	"	"
8 "	26.85	114.0	13.1	188.0	72.6	62.5	9.60	1.80	157.9	49.4	42.5	6.50	1.20	107.4	44.0	63.0	"	"
Lab. No. 2684.							**Bourbon Whiskey, Sour Mash.**											
New	47.58	101.0	0.0	13.9	11.9	53.2	0.79	....	116.8	12.0	53.7	0.8	....	118.0	0.0	....	...	...
1 year	....	102.0	5.4	76.0	51.8	55.9	7.5	0.588	122.5	50.6*	54.7*	7.28*	0.575*	119.7*	13.6	46.0	Neg	Neg
2 years	....	103.0	7.52	94.0	60.6	59.8	7.7	0.777	126.2	57.0*	56.3*	7.31*	0.731*	118.8*	44.6	....	"	"
3 "	....	103.7	8.92	119.0	64.8	73.0	8.80	1.00	134.0	58.7*	66.1*	8.03*	0.873*	121.3*	40.0	56.0	"	"
4 "	....	104.8	9.50	133.0	....	79.8	11.1	1.10	134.5	....	69.6*	9.65*	0.917*	117.3*	32.0	....	"	"
5 "	....	106.0	11.8	153.0	64.5	79.7	11.7	1.00	135.9	54.0*	66.7*	9.80*	0.869*	113.7*	38.0	60.0	"	"
6 "	....	108.0	12.0	155.0	73.3	83.9	11.4	1.10	138.9	59.2*	67.8*	9.27*	0.898*	112.0*	40.0	....	"	"
7 "	33.55	109.6	12.3	173.0	78.8	87.7	11.8	1.18	146.0	60.9	68.0	9.16	0.916	113.0	44.0	64.0	"	"
8 "	32.52	109.8	12.3	176.0	83.0	87.3	12.0	1.30	149.4	62.3	65.6	9.00	0.900	112.1	44.0	55.0	"	"

TABLE X.

Time in wood.	Wine gallons in barrel.	Proof.	Color calculated to 100 proof.	Grams per 100 liters of 100 proof spirit. Solids.	Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural	Fusel oil as amyl alcohol.	Grams per 100 liters calculated to original volume. Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Color removed by ether.	Color insoluble in water.	Caramel color. Paraldehyde test.	Marsh test.
Lab. No. 2685. BOURBON WHISKEY, SOUR MASH.																		
New	47.14	101.0	0.0	18.0	....	....	....	....	97.0	....	....	....	....	98.0	0.0	....	...	...
1 year	....	101.5	7.64	96.0	33.1	41.5	2.76	....	137.9	31.7*	39.8*	2.64*	....	132.1*	12.9	54.0	Neg	Neg
2 years	....	103.0	10.92	119.0	44.3	54.7	1.16	0.87	128.2	40.9*	50.4*	1.07*	0.806*	118.3*	42.7	....	"	"
3 "	....	105.5	12.3	145.0	52.3	54.2	13.3	1.2	155.4	46.6*	48.3*	11.8*	1.00*	138.6*	40.0	61.0	"	"
4 "	....	106.5	14.1	163.0	58.6	58.7	14.3	1.3	144.6	49.7*	49.8*	12.1*	1.11*	122.6*	33.0	....	"	"
5 "	....	109.0	16.0	200.0	72.0	60.5	15.2	1.4	141.3	53.2*	49.1*	12.4*	1.12*	114.6*	32.0	66.0	"	"
6 "	....	109.5	18.2	213.0	69.0	69.0	15.3	1.2	173.5	52.5*	52.5*	11.7*	0.97*	131.8*	37.0	....	"	"
7 "	30.25	111.0	18.9	237.0	60.9	69.0	15.3	1.6	162.2	49.3	49.4	10.9	1.16	115.6	38.0	65.0	"	"
8 "	27.81	112.0	19.6	236.0	76.1	68.4	15.7	1.8	180.3	50.2	45.2	10.3	1.10	119.2	44.0	65.0	"	"
Lab. No. 2686. BOURBON WHISKEY, SOUR MASH.																		
New	48.22	101.5	0.0	18.0	alk.	13.9	3.9	....	185.2	alk.	14.1	4.0	....	188.0	0.00	....	...	...
1 year	....	102.0	9.07	112.0	24.7	46.6	8.23	1.17	172.5	23.7*	44.7*	7.91*	1.03*	165.8*	13.5	41.0	Neg	Neg
2 years	....	103.5	11.35	147.0	61.4	54.4	8.69	1.17	197.1	56.3*	54.5*	7.96*	1.15*	181.0*	40.7	....	"	"
3 "	....	105.5	12.3	175.0	68.2	54.2	10.2	1.20	221.8	59.6*	47.4*	8.94*	1.08*	193.8*	42.8	67.0	"	"
4 "	....	108.0	13.9	185.0	73.0	80.6	11.1	1.40	237.1	57.9*	67.2*	9.26*	1.16*	197.6*	37.0	....	"	"
5 "	....	111.0	15.3	195.0	78.9	87.2	11.5	1.40	243.4	62.6*	69.2*	9.15*	1.14*	193.1*	40.0	69.0	"	"
6 "	....	114.0	16.7	223.0	81.0	87.2	11.9	1.40	226.3	60.8*	65.4*	8.95*	1.05*	169.7*	44.0	....	"	"
7 "	28.95	116.7	17.6	248.0	86.4	90.0	12.0	1.37	243.4	60.5	63.4	8.45	0.96	170.7	43.0	73.0	"	"
8 "	26.50	120.7	17.8	252.0	91.4	92.1	11.6	1.50	241.8	60.6	61.1	7.70	1.00	160.5	42.0	62.0	"	"
Lab. No. 2689. BOURBON WHISKEY, SOUR MASH.																		
New	49.20	100.0	1.25	161.0	1.2	1.3	4.0	trace	42.0	1.20	1.30	4.00	trace	42.0	40.0	....	...	...
1 year	....	101.0	7.90	193.0	....	....	....	0.99	42.8	....	....	...	0.953*	41.0*	40.0	....	...	...
2 years	44.63	101.0	10.9	214.0	25.5	11.2	5.9	1.0	42.8	23.4	10.3	5.4	0.900	39.0	12.0	14.0	...	...
3 "	43.08	101.0	12.9	245.0	32.1	12.1	5.9	1.0	43.5	28.4	10.7	5.2	0 900	38.5	25.9	13.0	...	...
4 "	....	101.0	14.8	249.0	40.4	13.8	6.9	0.99	43.5	33.8*	11.6*	5.8*	0.828*	36.4*	19.0	....	...	...
5 "	....	102.0	16.7	280.0	48.2	17.3	7.0	0.98	45.1	38.4*	13.4*	5.8*	0.780*	35.9*	23 0	9.0	...	...
6 "	35.91	103.0	17.5	287.0	53.6	17.9	7.7	1.0	44.6	40.2	13.4	5.8	0.730	33.6	22.0	....	...	...
7 "	....	103.0	19.4	309.0	60.6	21.3	7.7	0.97	46 6	44.5*	15.7*	5.7*	0.714*	34.3*	22.0	9.0	...	...
8 "	34.34	103.0	20.9	326.0	64.1	22.1	8.7	1.00	47.6	46.0	15.9	6.2	0.700	34.2	28.0	22.0	...	...

TABLE IX.

Time in wood.	Wine gallons in barrel.	Proof.	Color calculated to 100 proof.	Grams per 100 liters of 100 proof spirit. Solids.	Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Grams per 100 liters, calculated to original volume. Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Color removed by ether.	Color insoluble in water.	Caramel color. Paraldehyde test.	Marsh test.
Lab. No. 2644. BOURBON WHISKEY, SOUR MASH.																		
New	47.94	103.5	0.0	9.00	3.4	11.9	2.3	....	74.4	3.6	12.3	2.4	....	77.0	0.0	....	...	...
1 year	....	102.5	4.63	65.0	26.3	17.2	3.5	0.98	83.9	25.8*	16.8*	3.4*	0.095*	82.3*	10.5	57.0	Neg	Neg
2 years	....	101.0	5.69	85.0	34.4	33.0	9.90	0.800	87.1	31.8*	30.5*	9.14*	0.731*	80.4*	43.5	50.0	"	"
3 "	....	100.0	7.00	99.0	38.4	31.7	11.20	0.800	88.0	33.5*	27.6*	9.76*	0.697*	82.8*	40.0	58.0	"	"
4 "	....	101.0	7.40	101.0	40.4	34.8	12.3	1.00	103.9	33.9*	29.2*	10.3*	0.996*	88.8*	38.0	....	"	"
5 "	....	101.0	8.40	125.0	42.7	35.7	12.7	1.20	105.9	34.0*	28.5*	9.54*	0.946*	84.3*	36.0	56.0	"	"
6 "	....	101.6	9.30	132.0	45 0	36.4	12.6	1.00	108.2	34.1*	27.6*	9.55*	0.746*	82.1*	41.0	....	"	"
7 "	33.75	102.0	10.05	147.0	49.0	37.1	12.7	0.98	106.8	35.4	27.1	9.14	0.703	76.7	39.0	63.0	"	"
8 "	32.73	102.7	10.45	152.0	53.7	37.7	13.6	1.20	106.1	37.6	26.4	9.50	0.800	74.4	37.0	58.0	"	"
Lab. No. 2683. BOURBON WHISKEY, SOUR MASH.																		
New	45.0	103.0	0.0	5.0	16.3	25.6	1.9	none	114.6	16.8	26 4	2.0	none	118.0	0.0	....	...	...
1 year	....	102.0	10.9	88.0	42.3	26.5	7.8	0.59	119.6	40.8*	25.5*	7.52*	0.56*	115.0*	11.1	30.0	Neg	Neg
2 years	....	103.0	8.98	110.0	47.8	47.0	8.10	1.40	122.3	44.8*	43.4*	7.52*	1.25*	112.8*	42.5	63.0	"	"
3 "	....	104.0	9.37	122.0	53.0	48.3	9.20	1.50	121.1	46.6*	42.4*	8.11*	1.35*	106.4*	40.0	63.0	"	"
4 "	....	105.0	9.50	130.0	54.9	49.3	9.5	1.5	133.3	45.9*	41.1*	7.96*	1.27*	111.4*	41.0	....	"	"
5 "	....	107.0	12.1	149.0	54.6	51.8	9.30	1.60	149.5	43.4*	41.2*	7.44*	1.26*	119.0*	42.0	62.0	"	"
6 "	....	108.6	13.4	151.0	63.0	55.0	9.90	1.70	149.3	47.5*	41.5*	7.49*	1.25*	112.4*	43.0	....	"	"
7 "	28.89	112.0	13.8	171.0	62.1	62.8	9.8	1.6	148.2	44.7	45.2	7.06	1.16	106.6	43.0	64.0	"	"
8 "	26.85	114.0	13.1	188.0	72.6	62.5	9.60	1.80	157.9	49.4	42.5	6.50	1.20	107.4	44.0	63.0	"	"
Lab. No. 2684. BOURBON WHISKEY, SOUR MASH.																		
New	47.58	101.0	0.0	13.9	11.9	53.2	0.79	....	116.8	12.0	53.7	0.8	....	118.0	0.0	....	...	...
1 year	....	102.0	5.4	76.0	51.8	55.9	7.5	0.588	122.5	50.6*	54.7*	7.28*	0.575*	119.7*	13.6	46.0	Neg	Neg
2 years	....	103.0	7.52	94.0	60.6	59.8	7.7	0.777	126.2	57.0*	56.3*	7.31*	0.731*	118.8*	44.6	....	"	"
3 "	....	103.7	8.92	119.0	64.8	73.0	8.80	1.00	134.0	58.7*	66.1*	8.03*	0.873*	121.3*	40.0	56.0	"	"
4 "	....	104.8	9.50	133.0	....	79.8	11.1	1.10	134.5	....	69.6*	9.65*	0.917*	117.3*	32.0	....	"	"
5 "	....	106.0	11.8	153.0	64.5	79.7	11.7	1.00	135.9	54.0*	66.7*	9.80*	0.869*	113.7*	38.0	60.0	"	"
6 "	....	108.0	12.0	155.0	73.3	83.9	11.4	1.10	138.9	59.2*	67.8*	9.27*	0.898*	112.0*	40.0	....	"	"
7 "	33.55	109.6	12.3	173.0	78.8	87.7	11.8	1.18	146.0	60.9	68.0	9.16	0.916	113.0	44.0	64.0	"	"
8 "	32.52	109.8	12.3	176.0	83.0	87.3	12.0	1.30	149.4	62.3	65.6	9.00	0.900	112.1	44.0	55.0	"	"

TABLE X.

Time in wood.	Wine gallons in barrel.	Proof.	Color calculated to 100 proof.	Grams per 100 liters of 100 proof spirit. Solids.	Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural	Fusel oil as amyl alcohol.	Grams per 100 liters calculated to original volume. Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Color removed by ether.	Color insoluble in water.	Caramel color. Paraldehyde test.	Marsh test.
Lab. No. 2685.							**BOURBON WHISKEY, SOUR MASH.**											
New	47.14	101.0	0.0	18.0	....	....	....	....	97.0	....	....	....	....	98.0	0.0	....	...	...
1 year	....	101.5	7.64	96.0	33.1	41.5	2.76	....	137.9	31.7*	39.8*	2.64*	....	132.1*	12.9	54.0	Neg	Neg
2 years	....	103.0	10.92	119.0	44.3	54.7	1.16	0.87	128.2	40.9*	50.4*	1.07*	0.806*	118.3*	42.7	....	"	"
3 "	....	105.5	12.3	145.0	52.3	54.2	13.3	1.2	155.4	46.6*	48.3*	11.8*	1.00*	138.6*	40.0	61.0	"	"
4 "	....	106.5	14.1	163.0	58.6	58.7	14.3	1.3	144.6	49.7*	49.8*	12.1*	1.11*	122.6*	33.0	....	"	"
5 "	....	109.0	16.0	200.0	72.0	60.5	15.2	1.4	141.3	53.2*	49.1*	12.4*	1.12*	114.6*	32.0	66.0	"	"
6 "	....	109.5	18.2	213.0	69.0	69.0	15.3	1.2	173.5	52.5*	52.5*	11.7*	0.97*	131.8*	37.0	....	"	"
7 "	30.25	111.0	18.9	237.0	60.9	69.0	15.3	1.6	162.2	49.3	49.4	10.9	1.16	115.6	38.0	65.0	"	"
8 "	27.81	112.0	19.6	236.0	76.1	68.4	15.7	1.8	180.3	50.2	45.2	10.3	1.10	119.2	44.0	65.0	"	"
Lab. No. 2686.							**BOURBON WHISKEY, SOUR MASH.**											
New	48.22	101.5	0.0	18.0	alk.	13.9	3.9	....	185.2	alk.	14.1	4.0	....	188.0	0.00	....	...	...
1 year	....	102.0	9.07	112.0	24.7	46.6	8.23	1.17	172.5	23.7*	44.7*	7.91*	1.03*	165.8*	13.5	41.0	Neg	Neg
2 years	....	103.5	11.35	147.0	61.4	54.4	8.69	1.17	197.1	56.3*	54.5*	7.96*	1.15*	181.0*	40.7	....	"	"
3 "	....	105.5	12.3	175.0	68.2	54.2	10.2	1.20	221.8	59.6*	47.4*	8.94*	1.08*	193.8*	42.8	67.0	"	"
4 "	....	108.0	13.9	185.0	73.0	80.6	11.1	1.40	237.1	57.9*	67.2*	9.26*	1.16*	197.6*	37.0	....	"	"
5 "	....	111.0	15.3	195.0	78.9	87.2	11.5	1.40	243.4	62.6*	69.2*	9.15*	1.14*	193.1*	40.0	69.0	"	"
6 "	....	114.0	16.7	223.0	81.0	87.2	11.9	1.40	226.3	60.8*	65.4*	8.95*	1.05*	169.7*	44.0	....	"	"
7 "	28.95	116.7	17.6	248.0	86.4	90.0	12.0	1.37	243.4	60.5	63.4	8.45	0.96	170.7	43.0	73.0	"	"
8 "	26.50	120.7	17.8	252.0	91.4	92.1	11.6	1.50	241.8	60.6	61.1	7.70	1.00	160.5	42.0	62.0	"	"
Lab. No. 2689.							**BOURBON WHISKEY, SOUR MASH.**											
New	49.20	100.0	1.25	161.0	1.2	1.3	4.0	trace	42.0	1.20	1.30	4.00	trace	42.0	40.0	....	...	...
1 year	....	101.0	7.90	193.0	....	....	....	0.99	42.8	....	....	...	0.953*	41.0*	40.0	....	...	...
2 years	44.63	101.0	10.9	214.0	25.5	11.2	5.9	1.0	42.8	23.4	10.3	5.4	0.900	39.0	12.0	14.0	...	...
3 "	43.08	101.0	12.9	245.0	32.1	12.1	5.9	1.0	43.5	28.4	10.7	5.2	0 900	38.5	25.9	13.0	...	...
4 "	....	101.0	14.8	249.0	40.4	13.8	6.9	0.99	43.5	33.8*	11.6*	5.8*	0.828*	36.4*	19.0	....	...	...
5 "	....	102.0	16.7	280.0	48.2	17.3	7.0	0.98	45.1	38.4*	13.4*	5.8*	0.780*	35.9*	23 0	9.0	...	...
6 "	35.91	103.0	17.5	287.0	53.6	17.9	7.7	1.0	44.6	40.2	13.4	5.8	0.730	33.6	22.0	....	...	...
7 "	....	103.0	19.4	309.0	60.6	21.3	7.7	0.97	46 6	44.5*	15.7*	5.7*	0.714*	34.3*	22.0	9.0	...	...
8 "	34.34	103.0	20.9	326.0	64.1	22.1	8.7	1.00	47.6	46.0	15.9	6.2	0.700	34.2	28.0	22.0	...	...

TABLE XI.

Time in wood.	Wine gallons in barrel.	Proof.	Color calculated to 100 proof.	Solids.	Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Color removed by ether.	Color insoluble in water.	Paraldehyde test.	Marsh test.
				Grams per 100 liters of 100 proof spirit.						Grams per 100 liters calculated to original volume.							Caramel color.	
Lab. No. 2689 *a*.							BOURBON WHISKEY, SOUR MASH.											
New.....	47.26	102.0	2.20	80.0	4.70	7.7	6.80	0.50	141.0	4.80	7.9	7.00	0.500	144.0	22 2	....	...	...
1 year	....	102.0	7.60	131.0	30.6	4.30	3.90	1.00	149.0	29.6*	4.18*	3.86*	0.955*	144.0*	19.3	13.0	Neg	...
2 years.....	....	101.0	9.16	156.0	41.6	24.4	10.3	0.99	152.5	37.9*	22.1*	9.35*	0.899*	138.4*	35.0	....	"	Neg
3 "	....	100.0	11.5	177.0	48.0	27.2	11.0	1.2	156.0	42.5*	24.1*	9.73*	1.06*	138.1*	40.0	19.0	"	"
4 "	41.0	100.0	12.5	184.0	55.8	28.2	11.0	1.50	162.0	48.4	24.4	9.50	1.30	140.6	28.0	....	"	"
5 "	....	102.6	12.2	203.0	59.6	27.7	10.9	1.36	157.9	50.6*	23.5*	9.26*	1.16*	134.0*	34.0	26.0	"	"
6 "	....	102.7	13.6	218.0	64.0	39.4	11.1	1.50	177.2	51.9*	31.9*	8.97*	1.18*	143.2*	36.0	....	"	"
7 "	34.25	104.6	14.8	235.0	70.5	46.2	11.4	1.90	187.3	53.4	35.0	8.70	1.40	142.0	33.0	33.0	"	"
8 "	34.0	102.0	15.2	230.0	70.6	40.5	11.7	2.90	194.1	51.7	29.7	8.60	2.10	142.3	33.0	19.0	"	"

TABLE XII.

Time in wood.	Wine gallons in barrel.	Proof.	Color calculated to 100 proof.	Grams per 100 liters of 100 proof spirit. Solids.	Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Grams per 100 liters calculated to original volume. Acids as acetic.	Esters as acetic.	Aldehydes as acetic.	Furfural.	Fusel oil as amyl alcohol.	Color removed by ether.	Color insoluble in water.	Caramel color. Paraldehyde test.	Marsh test.
Lab. No. 2625.							BOURBON WHISKEY, SOUR MASH.											
New	45.6	101.0	0.0	21.0	1.20	6.10	3.00	2.00	71.3	1.20	6.10	3.00	2.00	72.0	0.0	....	...	...
1 year	....	100.0	2.75	61.0	7.20	23.7	7.00	2.50	58.0	6.89*	22.7*	6.70*	2.39*	55.5*	13.4	....	...	Neg
2 years	....	100.0	4.50	81.0	49.2	44.0	9.00	2.50	92.0	45.2*	40.4*	8.26*	2.29*	84.4*	37.5	....	Neg	"
3 "	....	100.0	4.75	95.0	62.4	....	....	3.00	....	54.9*	....	....	2.64*	....	40.0	....	?	...
4 "	....	101.0	5.00	101.0	70.7	59.2	9.9	2.97	115.0	60.0*	50.2*	8.4*	2.52*	97.4*	19.0	....	Neg	Neg
5 "	....	102.0	6.00	120.0	73.5	70.7	10.8	2.94	119.6	60.0*	57.6*	8.8*	2.40*	97.6*	24.0	....	"	"
6 "	....	103.0	6.5	132.0	79.2	71.7	11.6	2.90	130.1	62.6*	56.1*	9.12*	2.28*	102.0*	23.0	....	...	...
7 "	33.03	103.0	6.75	140.0	85.0	76.0	11.7	3.20	99.0	63.1	57.1	8.64	2.38	86.4	26.0	....	Neg	Neg
8 "	30.35	103.0	6.75	153.0	90.9	78.5	12.0	3.40	110.7	62.3	53.8	8.20	2.30	75.8	26.0	....	...	...
Lab. No. 2627.							BOURBON WHISKEY, SOUR MASH.											
New	46.5	101.0	0.0	11.9	11.9	34.0	3.9	0.59	83.2	12.0	34.3	4.0	0.6	84.0	0.0	....	...	...
1 year	....	101.6	2.50	54.0	25.5	35.7	5.9	0.98	84.6	25.7*	36.0*	5.7*	0.95*	82.0*	8.3	....	...	...
2 years	....	102.0	3.90	78.0	43.5	50.0	6.30	1.00	86.2	40.3*	46.3*	5.80*	0.907*	79.8*	9.3	....	...	...
3 "	....	103.0	4.13	90.0	50.1	57.2	7.00	1.10	96.2	44.4*	50.7*	6.20*	0.947*	85.2*	12.5	....	...	...
4 "	....	104.0	4.30	92.0	56.2	64.0	7.70	1.20	97.1	....	53.8*	6.53*	0.978*	82.3*	29.0	....	...	...
5 "	....	105.0	5.70	114.0	57.1	56.1	7.60	1.30	100.0	46.2*	45.4*	6.16*	1.00*	80.8*	28.0	8.0	...	...
6 "	....	107.0	5.80	127.0	62.8	63.4	9.30	1.40	98.1	48 7*	49.1*	7.25*	1.01*	76.1*	32.0	....	...	...
7 "	31.65	109.0	6.2	134.0	66.1	67.8	10.1	1.38	98.2	49.0	50.1	7.46	1.02	72.6	33.0	22.0	...	...
8 "	29.89	110.9	6.3	141.0	73.5	76.1	9.73	1.40	101.0	52.4	54.3	6.90	1.00	72.0	35.0	23.0	...	...

Whiskey Aged in Uncharred Packages.

No. 2627 (see Table XII): Sour mash, Bourbon whiskey, entered into bonded warehouse February 5, 1898, in a new, uncharred, white oak, seasoned barrel (4 years old); warehouse, dry and above ground; average temperature in the winter 42°, in the summer 80°. Composition of the mash: malt, 6,048 pounds; rye, 4,704 pounds; corn, 45,024 pounds. The spirit was distilled in a copper still of 5,182 gallons capacity, connected with a second still of 2,133 gallons capacity, and with a doubler of a capacity of 950 gallons. The spirit is taken directly from the doubler to the cistern-room without rectification or filtration. Yield per bushel of grain, 4 gallons. The flavor is rank, even in eight-year old goods, and very different from that of all samples aged in charred wood.

No. 2625 (see Table XII): Sour mash, Bourbon whiskey, entered into bonded warehouse January 31, 1898, in a new, uncharred, white oak barrel; low-boxed warehouse, about three feet from the ground; average temperature in winter 48°, in the summer 80°. Composition of the mash: malt, 952 pounds; rye, 448 pounds; corn, 8,400 pounds. Distilled from a column still, capacity 150 gallons per hour. No leach tubes used. Yield, 4 gallons of proof spirit per bushel of grain. Flavor not so rank as No. 2627. Odor, not like any American whiskey.

TABLE XIII.—AVERAGE, MAXIMA AND MINIMA DATA ON ALL THE SAMPLES OF WHISKEY.

Grams per 100 liters, 100 proof spirit.

Age.	Data for 31 samples.	Proof.	Color.	Solids.	Acids.	Esters.	Aldehydes.	Furfural.	Fusel oil.
New	Average	101.9	....	20.1	6.4	16.3	3.9	0.9	95.2
	Maximum	104.0	....	161.0	29.1	53.2	15.0	2.0	171.3
	Minimum	100.0	....	5.0	1.2	1.3	trace	trace	42.0
1 yr.	Average	102.0	8.2	109.4	43.6	32.6	6.7	1.7	110.7
	Maximum	104.0	13.8	193.0	60.5	64.8	15.5	7.9	194.0
	Minimum	100.0	4.6	54.0	5.8	6.8	1.5	0.2	42.8
2 yrs.	Average	103.6	10.1	135.0	48.6	46.6	9.3	1.8	114.0
	Maximum	109.0	16.7	214.0	63.0	75.1	18.7	9.1	214.0
	Minimum	100.0	5.7	78.0	11.0	11.2	5.9	0.4	42.8
3 yrs.	Average	105.2	11.7	160.1	58.5	54.8	11.5	2.1	121.2
	Maximum	112.0	18.3	245.0	81.8	83.9	22.1	9.5	202.0
	Minimum	100.0	7.0	90.0	16.4	12.1	5.9	0.6	43.5
4 yrs.	Average	107.6	12.4	167.9	62.2	61.1	12.4	2.3	125.8
	Maximum	118.0	18.9	249.0	83.8	89.1	22.2	9.6	237.1
	Minimum	100.0	7.4	92.0	17.3	13.8	6.4	0.7	43.5
5 yrs.	Average	109.8	14.1	189.0	64.6	65.0	13.1	2.5	126.8
	Maximum	125.0	19.2	280.0	92.6	105.5	23.1	9.6	254.2
	Minimum	101.0	8.4	114.0	19.0	17.3	6.6	0.8	45.1
6 yrs.	Average	112.8	15.0	203.5	69.7	69.5	13.1	2.6	139.9
	Maximum	132.0	21.2	287.0	96.8	109.0	23.7	9.5	245.3
	Minimum	102.0	9.3	132.0	24.3	17.9	7.5	0.7	44.6
7 yrs.	Average	115.3	15.9	220.9	74.3	73.0	13.8	2.5	141.0
	Maximum	141.0	22.7	309.0	100.0	114.9	26.7	8.5	264.5
	Minimum	102.0	10.1	134.0	24.7	21.3	7.5	0.8	46.6
8 yrs.	Average	117.0	16.3	231.6	79.4	76.6	14.3	2.7	148.8
	Maximum	134.0	24.2	326.0	112.0	126.6	28.8	10.0	280.3
	Minimum	102.0	10.5	141.0	31.7	22.1	7.9	0.8	47.6

Discussion of Table XIII.

This table shows the average, maxima, and minima data for each year on all of the thirty-one samples, with the exception that the fusel oil results on Sample No. 2612, which was practically cologne spirits and the results obtained on the color and solids of samples Nos. 2625 and 2627, which were aged in uncharred packages, were omitted.

The maximum and minimum figures alone have little value except to show the range obtained, because they do not establish any relationship between the various substances, as is done by the average figures.

One would not be justified in using these maximum and minimum limits in judging the purity of the whiskey, because the results show that in a properly matured spirit the maximum in color and solids, for instance, does not occur with a minimum of acids and esters, so that if a sample of commercial whiskey should show a maximum color, it should not show the minimum acids and esters, and if such a condition were found, it would indicate that the product was a compounded article.

In the discussion of the analysis of a whiskey, all of the determinations and their relations must be considered before making a decision as to its purity. The simple fact that it falls between the limits shown by the maxima and minima figures is alone no definite indication as to its genuineness.

An interesting study might be made of the conditions which brought about these extreme results, which would be of practical value to the industry, but such discussion is beyond the scope of this paper. The facts alone will be presented, so that any one who is interested may interpret them.

It is evident from this work that there are two sources of furfural in whiskey. This is shown by the fact that some of the new distillates contain mere traces, while the mature spirits from the same source have considerable amounts, indicating that it must have been derived from the barrel; again, other samples of the fresh distillate contain considerable amounts, indicating that it must have come over in distillation and been derived from the grain of the mash. All of the samples, however, when calculated to the original (see Table 15) showed a slight increase of furfural on aging, which was undoubtedly derived from the charred wood.

Discussion of Table XIV.

This table gives the average, maximum and minimum of the determinations made on the rye whiskies.

The maxima, except on the color and solids, are of little value in judging the purity of other whiskies. These maxima for the various years give us limits for color and solids which will rarely be exceeded, and as shown by the average will be, as a rule, much less. The close relation-

ship which should obtain between solids and color is shown by this chart. The sample showing the maximum color in each year also contains the maximum solids, except in the sixth year, where there is another sample showing slightly higher solids.

TABLE XIV.—AVERAGE, MAXIMA AND MINIMA DATA ON RYE WHISKIES.

Calculated to 100 proof.

Age.	Data.	Original proof.	Color.	Solids.	Acids.	Esters.	Aldehydes.	Furfural.	Fusel oil.
New	Average.....	101.2	0.0	13.3	4.4	16.3	5.4	1.0	90.4
	Maximum...	102.0	0.0	30.0	72.0	21.8	15.0	1.9	161.8
	Minimum....	100.0	0.0	5.0	12.0	4.3	0.7	trace	61.8 43.7
1 yr.	Average.....	102.5	8.8	119.7	46.6	37.0	7.0	1.8	111.5
	Maximum...	104.0	13.8	171.0	60.5	64.8	15.5	3.3	194.0
	Minimum....	101.0	7.2 6.6	93.0 92.0	33.1 5.8	6.8 6.8	2.8	0.4	80.4 66.4
2 yrs.	Average.....	104.9	11.6	144.7	51.9	54.0	10.5	2.2	112.4
	Maximum...	109.0	16.7	199.0	75.6	75.1	18.7	5.7	214.0
	Minimum....	100.0	8.8 8.6	121.0 94.0	44.3 11.0	41.5 31.2	5.4	0.7	83.4 82.2
3 yrs.	Average.....	107.7	13.2	171.4	62.7	61.5	12.5	1.5	112.7
	Maximum..	112.0	18.3	224.0	81.8	79.8	20.8	6.1	202.0
	Minimum....	104.0	11.4 10.1	145.0 119.0	52.3 16.4	47.6 34.3	6.5	0.7	79.0 60.0
4 yrs.	Average.....	111.2	14.0	185.0	65.9	69.3	13.9	2.8	125.1
	Maximum...	118.0	18.9	238.0	83.8	89.1	22.1	6.7	203.5
	Minimum....	105.0	11.6 11.3	156.0 153.0	58.6 17.3	57.7 36.3	6.4	0.7	83.8 67.8
5 yrs.	Average.....	113.8	15.9	206.5	67.6	75.0	15.0	3.2	128.1
	Maximum...	125.0	19.2	251.0	92.6	105.5	22.4	7.7	254.2
	Minimum....	108.0	13.2 11.8	170.0 168.0	59.4 19.0	60.5 37.0	6.6	1.4	86.8 78.5
6 yrs.	Average.....	118.0	17.0	223.1	72.4	80.4	14.6	3.3	145.5
	Maximum...	132.0	21.2	284.0	95.8	109.0	22.3	8.3	245.3
	Minimum....	110.0	13.7 12.4	193.0 176.0	67.1 24.3	64.0 39.1	7.3	0.7	99.2 80.0
7 yrs.	Average	121.4	18.0	242.2	76.7	84.2	15.5	3.2	145.2
	Maximum...	141.0	22.7	306.0	100.0	114.9	25.2	8.5	264.5
	Minimum....	111.0	14.6 13.1	195.0 194.0	60.9 24.7	64.6 41.8	7.5	0.8	99.2 86.2
8 yrs.	Average.....	123.8	18.6	256.0	82.9	89.1	16.0	3.4	154.2
	Maximum...	132.0	24.2	339.0	112.0	126.6	26.5	9.2	280.3
	Minimum....	112.0	13.8 13.7	214.0 200.0	73.7 31.7	68.4 40.9	7.9	0.8	109.0 107.1

The minima, however, are of considerable interest, not so much for color and solids as for the acids and esters. Taking the acids for instance, the minimum for each year is given by one package, No. 2623, which is abnormal in many ways, and omitting it from consideration the minimum

of acids for the first year would be 33.1, only slightly below the average; for the second year it would be 44.3, and so on.

In order to show this and to eliminate the abnormal, the next to the lowest figures for the color, solids, acids, esters, and fusel oils are also included in the table.

TABLE XIV*a*.—AVERAGE, MAXIMA AND MINIMA DATA FOR BOURBON WHISKIES.

Calculated to 100 proof.

Age.	Data.	Proof.	Color.	Solids.	Acids.	Esters.	Aldehydes.	Furfural.	Fusel oil.
New	Average....	101.1	0.0	26.5	10.0	18.4	3.2	0.7	100.9
	Maximum .	104.0	0.0	161.0	29.1	53.2	7.9	2.0	171.3
	Minimum ..	100.0	0.0	4.0	12.0	13.0	1.0	trace	*71.3* 42.0
1 yr.	Average....	101.8	7.1	99.6	41.1	28.6	5.8	1.6	110.1
	Maximum ..	103.0	10.9	193.0	55.3	55.9	8.6	7.9	173.4
	Minimum...	100.0	*5.4* 4.6	61.0 54.0	24.7 7.2	*17.2* 10.4	2.7	trace	*58.0* 42.8
2 yrs.	Average....	102.2	8.6	126.8	45.6	40.0	8.4	1.6	108.9
	Maximum ..	104.0	11.8	214.0	61.7	59.8	12.0	9.1	197.1
	Minimum...	100.0	6.9 5.7	81.0 78.0	*25.5* 23.3	*24.4* 11.2	5.9	0.4	*86.2* 42.8
3 yrs.	Average....	103.0	10.0	149.3	54.3	48.1	10.5	1.7	112.4
	Maximum ..	106.0	13.8	245.0	64.8	73.0	22.1	9.5	221.8
	Minimum...	100.0	8.9 7.0	*95.0* 90.0	38.4 32.1	*27.2* 12.1	5.9	0.6	*88.0* 43.5
4 yrs.	Average....	104.3	10.8	151.9	58.4	53.5	11.0	1.9	123.9
	Maximum ..	108.0	14.8	249.0	73.0	80.6	22.2	9.6	237.1
	Minimum...	100.0	8.6 7.4	101.0 92.0	40.4 40.4	*28.2* 13.8	6.9	0.8	*95.0* 43.5
5 yrs.	Average....	106.1	12.3	173.3	56.3	55.9	11.4	1.9	125.3
	Maximum ..	113.0	16.7	280.0	78.9	87.2	23.1	9.6	243.4
	Minimum...	101.0	11.8 8.4	*125.0* 114.0	*48.2* 42.7	27.7 17.3	7.1	0.8	*98.0* 45.1
6yrs.	Average....	107.9	13.1	185.1	67.1	64.0	11.9	1.8	135.3
	Maximum ..	116.0	17.5	287.0	81.0	83.9	23.3	9.5	240.0
	Minimum...	102.0	12.0 9.8	132.0 127.0	53.6 45.0	*36.4* 17.9	7.7	0.9	*98.1* 44.6
7 yrs.	Average....	109.6	13.9	200.9	71.9	63.3	12.4	1.9	137.2
	Maximum ..	120.0	19.4	309.0	86.4	90.0	26.7	8.3	243.4
	Minimum...	103.0	11.8 10.1	*140.0* 134.0	*60.6* 49.0	*37.1* 21.3	7.7	0.9	*98.2* 46.6
8 yrs.	Average....	111.1	14.2	210.3	76.4	65.6	12.9	2.1	143.5
	Maximum ..	124.0	20.9	326.0	91.4	93.6	28.8	10.0	241.8
	Minimum...	102.0	12.3 10.5	*152.0* 141.0	*64.1* 53.7	37.7 22.1	8.7	1.0	*110.0* 47.6

The point is especially noticable in the esters, for, omitting the minima, the lowest ester found on a four-year old whiskey was 57.7 grams, which is only slightly below the average, and would indicate that one might

expect in a four-year old rye whiskey 50 to 60 grams of esters to 100 liters.

Table XIV shows the average, maxima and minima data for the Bourbon whiskies.

The same may be said of this table as of the previous one in regard to the value of the maxima and minima figures.

All of these results indicate that we should expect lower figures with Bourbon whiskies than with rye.

The high solids shown in the maximum for the new spirit was due largely to ash, this being sample 2689, and the high ash changes, in this particular sample, the ratio between the color and solids.

TABLE XV.—AVERAGE DATA FOR ALL SAMPLES AND FOR RYE AND BOURBONS SEPARATELY.

Calculated to original volume.

Age.	Original volume.	Color.	Solids.	Acids.	Esters.	Aldehydes.	Furfural.	Fusel oil.
New	Whole.....	....	20.0	6.4	15.0	4.03	0.71	96.8
	Rye.....	....	13.6	4.7	13.7	4.91	0.97	83.2
	Bourbon.....	....	26.0	7.7	17.2	3.26	0.44	108.6
1 yr.	Whole.....	7.3	101.5	37.8	29.9	7.08	1.5	106.2
	Rye.....	8.4	114.6	41.8	35.3	8.71	1.7	106.8
	Bourbon.....	6.4	90.1	34.4	24.9	5.55	1.3	105.8
2 yrs.	Whole.....	8.6	124.2	46.1	42.9	8.34	1.7	108.1
	Rye.....	10.6	133.6	49.8	49.3	9.02	1.9	109.7
	Bourbon.....	6.7	114.8	42.7	37.3	7.78	1.4	107.3
3 yrs.	Whole.....	10.2	140.2	51.1	48.4	9.47	1.8	106.3
	Rye.....	11.5	150.4	54.4	54.3	9.80	2.2	104.4
	Bourbon.....	8.3	130.7	47.8	42.5	9.15	1.5	107.3
4 yrs.	Whole.....	10.2	140.4	51.6	50.9	10.2	1.9	104.3
	Rye.....	11.6	153.1	54.2	57.2	11.2	2.2	102.0
	Bourbon.....	8.9	127.7	48.9	45.0	9.3	1.5	106.3
5 yrs.	Whole.....	11.1	149.2	52.2	51.1	10.2	1.9	100.4
	Rye.....	12.2	158.8	54.8	57.5	11.3	2.5	100.1
	Bourbon.....	10.0	140.2	49.8	45.0	9.2	1.5	100.7
6 yrs.	Whole.....	11.1	151.4	53.2	50.7	10.2	1.9	104.7
	Rye.....	12.3	161.0	54.8	55.5	11.3	2.4	105.9
	Bourbon.....	10.1	142.5	51.8	45.2	9.1	1.4	103.8
7 yrs.	Whole.....	11.1	154.0	52.2	51.1	9.8	1.8	99.9
	Rye.....	12.0	161.3	51.9	56.6	10.6	2.2	98.8
	Bourbon.....	10.2	147.1	52.4	46.4	9.0	1.4	101.6
8 yrs.	Whole.....	10.5	155.2	53.1	50.9	9.6	1.8	98.0
	Rye.....	11.1	163.8	52.6	56.7	10.6	2.2	99.0
	Bourbon.....	10.0	147.7	53.6	45.9	8.8	1.5	97.1

This table gives the average of all the whiskies and the average of the rye and Bourbon separately, calculated back to the original volume, in order to eliminate the effects due to the concentration taking place while the spirit was stored. The more important points brought out by this table are brought out in the various charts. These figures show

more nearly the actual changes taking place, and prove that after the third year there is very little change in the amounts of the various substances present. As has been said before, the changes taking place in the whiskey after the third or fourth year are almost entirely due to the concentration which occurs.

These figures also show that the difference between rye and Bourbon whiskies holds good even when the results are corrected for loss of volume, proving that with the rye whiskies there has been a greater activity in the aging processes.

The fact that after the third year, the acids, esters, and aldehydes do not show any appreciable increase when corrected for loss in volume, does not necessarily mean that there is no formation of these substances in the barrel, as there may be some loss of them through the wooden walls of the barrel, with the alcohol and water which is constantly passing off; but the fact that they remain so constant in amount would indicate that these substances are left behind, in the same manner as the fusel oil and solids, by what might be called the selective action of the wooden membrane constituting the walls of the porous cell in which these products are stored.

Chart I shows the average of the changes taking place in the proof and the volume.

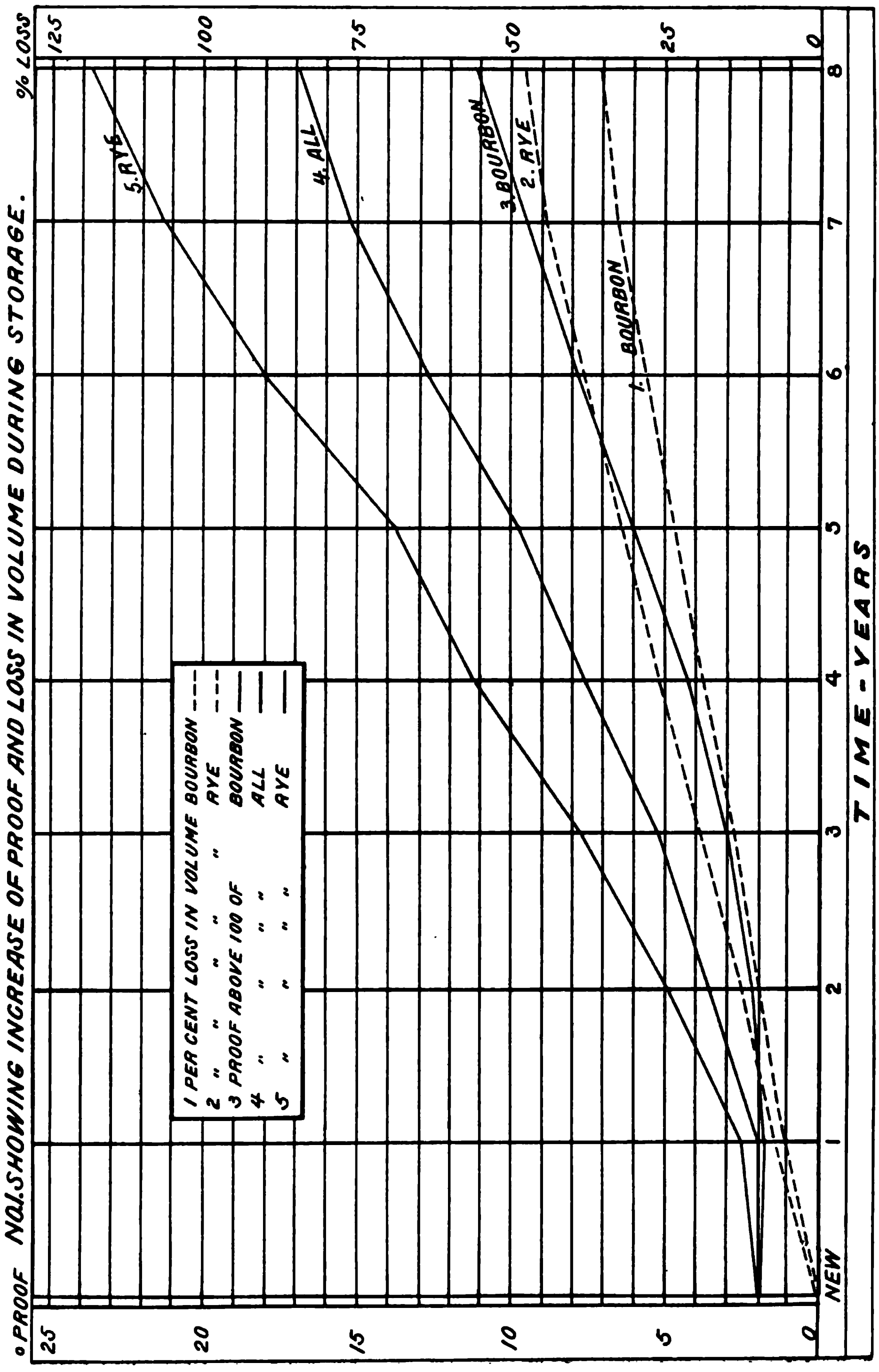
The proof increases, starting from approximately 100 proof, so that all that is shown on the curve are the degrees above 100 proof.

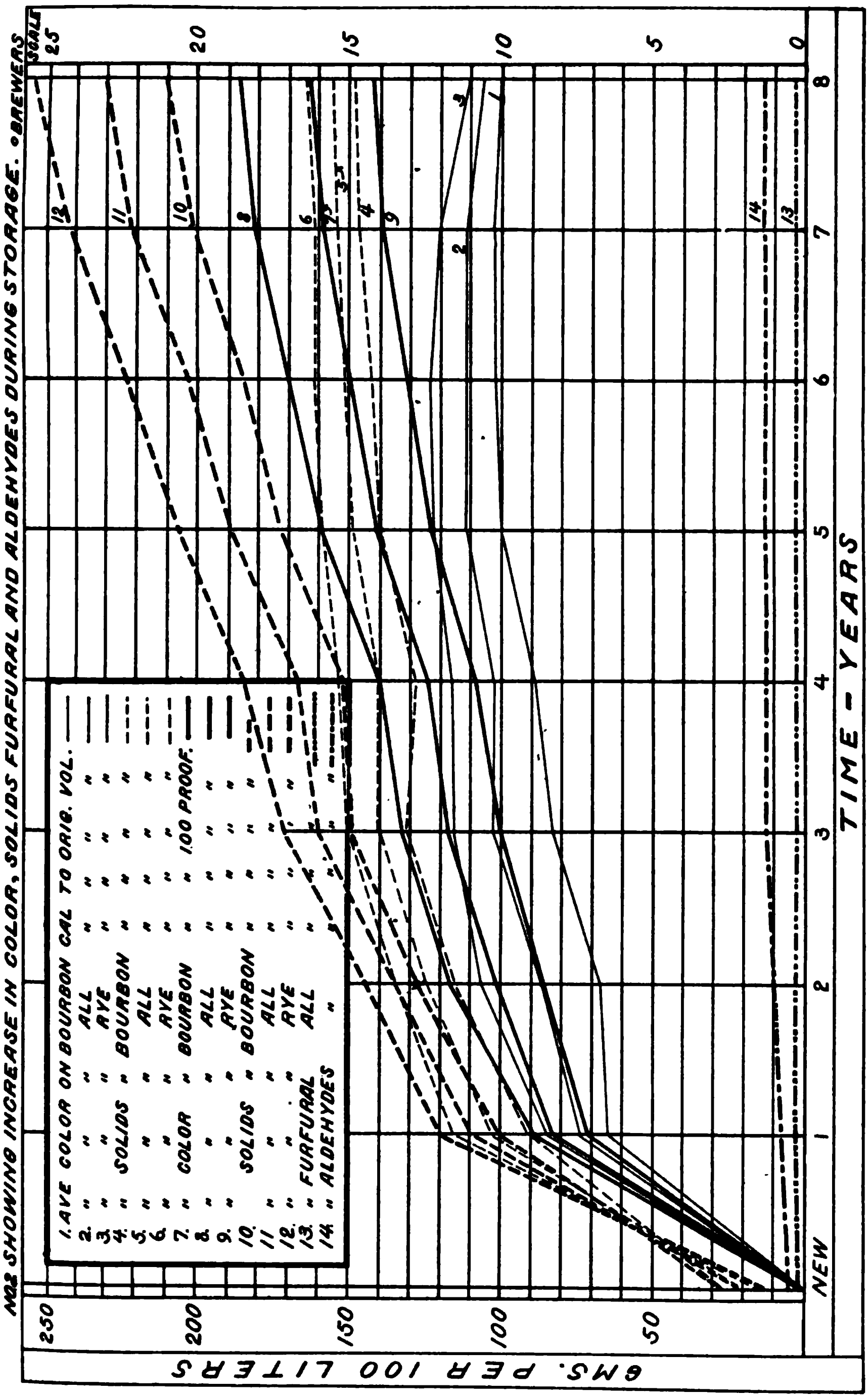
The changes in volume are plotted from the per cent. of loss in volume. The changes in proof and volume are important in their bearing on the changes that take place in the other substances.

The wide difference in rate of increase of proof shown by the rye and Bourbon whiskies is typical of the differences between them, and apparently has a simple explanation. In the case of the rye whiskies nearly all were aged in heated warehouses where the changes taking place are aided by the higher temperature. There is also a large loss of volume in the rye whiskies, as is shown by the lines. In short, there is much greater chemical activity, and so, greater changes. The amounts of acids and esters formed apparently have a direct relationship to the amount of the whiskey which passes through the wood of the barrel.

The Bourbon whiskies, on the other hand, are as a rule stored in unheated warehouses, so that there is less loss of volume in the spirit, and less increase in proof, and smaller amounts of acids and esters are formed. As a matter of fact, a much lighter bodied whiskey is formed, and from these results it would seem to be due to a greater extent to the method of storage than to the inherent differences in the whiskies themselves.

Chart II shows changes in solids and coloring matter, and the same differences between the rye and Bourbon whiskies as were noted on Chart


NOI. SHOWING INCREASE OF PROOF AND LOSS IN VOLUME DURING STORAGE.
% PROOF
% LOSS
TIME - YEARS
NEW
1
2
3
4
5
6
7
8
0
5
10
15
20
25
0
25
50
75
100
125
1 PER CENT LOSS IN VOLUME BOURBON
2 " " " RYE
3 PROOF ABOVE 100 OF BOURBON
4 " " " ALL
5 " " " RYE
1. BOURBON
2. RYE
3. BOURBON
4. ALL
5. RYE


MAP SHOWING INCREASE IN COLOR, SOLIDS FURFURAL AND ALDEHYDES DURING STORAGE. °BREWERS SCALE
1. AVE COLOR ON BOURBON CAL TO ORIG. VOL.
2. " " ALL " " " "
3. " " RYE " " " "
4. " SOLIDS " BOURBON " " " "
5. " " ALL " " " "
6. " " RYE " " " "
7. " COLOR " BOURBON " " " " 100 PROOF.
8. " " ALL " " " "
9. " " RYE " " " "
10. " SOLIDS " BOURBON " " " "
11. " " ALL " " " "
12. " " RYE " " " "
13. " FURFURAL ALL " " " "
14. " ALDEHYDES " " " "
GMS. PER 100 LITERS
250
200
150
100
50
25
20
15
10
5
0
NEW
1
2
3
4
5
6
7
8
TIME - YEARS

Whiskey Aged in Uncharred Packages.

No. 2627 (see Table XII): Sour mash, Bourbon whiskey, entered into bonded warehouse February 5, 1898, in a new, uncharred, white oak, seasoned barrel (4 years old); warehouse, dry and above ground; average temperature in the winter 42°, in the summer 80°. Composition of the mash: malt, 6,048 pounds; rye, 4,704 pounds; corn, 45,024 pounds. The spirit was distilled in a copper still of 5,182 gallons capacity, connected with a second still of 2,133 gallons capacity, and with a doubler of a capacity of 950 gallons. The spirit is taken directly from the doubler to the cistern-room without rectification or filtration. Yield per bushel of grain, 4 gallons. The flavor is rank, even in eight-year old goods, and very different from that of all samples aged in charred wood.

No. 2625 (see Table XII): Sour mash, Bourbon whiskey, entered into bonded warehouse January 31, 1898, in a new, uncharred, white oak barrel; low-boxed warehouse, about three feet from the ground; average temperature in winter 48°, in the summer 80°. Composition of the mash: malt, 952 pounds; rye, 448 pounds; corn, 8,400 pounds. Distilled from a column still, capacity 150 gallons per hour. No leach tubes used. Yield, 4 gallons of proof spirit per bushel of grain. Flavor not so rank as No. 2627. Odor, not like any American whiskey.

TABLE XIII.—AVERAGE, MAXIMA AND MINIMA DATA ON ALL THE SAMPLES OF WHISKEY.

Grams per 100 liters, 100 proof spirit.

Age.	Data for 31 samples.	Proof.	Color.	Solids.	Acids.	Esters.	Aldehydes.	Furfural.	Fusel oil.
New	Average	101.9	....	20.1	6.4	16.3	3.9	0.9	95.2
	Maximum	104.0	....	161.0	29.1	53.2	15.0	2.0	171.3
	Minimum	100.0	....	5.0	1.2	1.3	trace	trace	42.0
1 yr.	Average	102.0	8.2	109.4	43.6	32.6	6.7	1.7	110.7
	Maximum	104.0	13.8	193.0	60.5	64.8	15.5	7.9	194.0
	Minimum	100.0	4.6	54.0	5.8	6.8	1.5	0.2	42.8
2 yrs.	Average	103.6	10.1	135.0	48.6	46.6	9.3	1.8	114.0
	Maximum	109.0	16.7	214.0	63.0	75.1	18.7	9.1	214.0
	Minimum	100.0	5.7	78.0	11.0	11.2	5.9	0.4	42.8
3 yrs.	Average	105.2	11.7	160.1	58.5	54.8	11.5	2.1	121.2
	Maximum	112.0	18.3	245.0	81.8	83.9	22.1	9.5	202.0
	Minimum	100.0	7.0	90.0	16.4	12.1	5.9	0.6	43.5
4 yrs.	Average	107.6	12.4	167.9	62.2	61.1	12.4	2.3	125.8
	Maximum	118.0	18.9	249.0	83.8	89.1	22.2	9.6	237.1
	Minimum	100.0	7.4	92.0	17.3	13.8	6.4	0.7	43.5
5 yrs.	Average	109.8	14.1	189.0	64.6	65.0	13.1	2.5	126.8
	Maximum	125.0	19.2	280.0	92.6	105.5	23.1	9.6	254.2
	Minimum	101.0	8.4	114.0	19.0	17.3	6.6	0.8	45.1
6 yrs.	Average	112.8	15.0	203.5	69.7	69.5	13.1	2.6	139.9
	Maximum	132.0	21.2	287.0	96.8	109.0	23.7	9.5	245.3
	Minimum	102.0	9.3	132.0	24.3	17.9	7.5	0.7	44.6
7 yrs.	Average	115.3	15.9	220.9	74.3	73.0	13.8	2.5	141.0
	Maximum	141.0	22.7	309.0	100.0	114.9	26.7	8.5	264.5
	Minimum	102.0	10.1	134.0	24.7	21.3	7.5	0.8	46.6
8 yrs.	Average	117.0	16.3	231.6	79.4	76.6	14.3	2.7	148.8
	Maximum	134.0	24.2	326.0	112.0	126.6	28.8	10.0	280.3
	Minimum	102.0	10.5	141.0	31.7	22.1	7.9	0.8	47.6

Discussion of Table XIII.

This table shows the average, maxima, and minima data for each year on all of the thirty-one samples, with the exception that the fusel oil results on Sample No. 2612, which was practically cologne spirits and the results obtained on the color and solids of samples Nos. 2625 and 2627, which were aged in uncharred packages, were omitted.

The maximum and minimum figures alone have little value except to show the range obtained, because they do not establish any relationship between the various substances, as is done by the average figures.

One would not be justified in using these maximum and minimum limits in judging the purity of the whiskey, because the results show that in a properly matured spirit the maximum in color and solids, for instance, does not occur with a minimum of acids and esters, so that if a sample of commercial whiskey should show a maximum color, it should not show the minimum acids and esters, and if such a condition were found, it would indicate that the product was a compounded article.

In the discussion of the analysis of a whiskey, all of the determinations and their relations must be considered before making a decision as to its purity. The simple fact that it falls between the limits shown by the maxima and minima figures is alone no definite indication as to its genuineness.

An interesting study might be made of the conditions which brought about these extreme results, which would be of practical value to the industry, but such discussion is beyond the scope of this paper. The facts alone will be presented, so that any one who is interested may interpret them.

It is evident from this work that there are two sources of furfural in whiskey. This is shown by the fact that some of the new distillates contain mere traces, while the mature spirits from the same source have considerable amounts, indicating that it must have been derived from the barrel; again, other samples of the fresh distillate contain considerable amounts, indicating that it must have come over in distillation and been derived from the grain of the mash. All of the samples, however, when calculated to the original (see Table 15) showed a slight increase of furfural on aging, which was undoubtedly derived from the charred wood.

Discussion of Table XIV.

This table gives the average, maximum and minimum of the determinations made on the rye whiskies.

The maxima, except on the color and solids, are of little value in judging the purity of other whiskies. These maxima for the various years give us limits for color and solids which will rarely be exceeded, and as shown by the average will be, as a rule, much less. The close relation-

ship which should obtain between solids and color is shown by this chart. The sample showing the maximum color in each year also contains the maximum solids, except in the sixth year, where there is another sample showing slightly higher solids.

TABLE XIV.—AVERAGE, MAXIMA AND MINIMA DATA ON RYE WHISKIES.

Calculated to 100 proof.

Age.	Data.	Original proof.	Color.	Solids.	Acids.	Esters.	Aldehydes.	Furfural.	Fusel oil.
New	Average.....	101.2	0.0	13.3	4.4	16.3	5.4	1.0	90.4
	Maximum...	102.0	0.0	30.0	72.0	21.8	15.0	1.9	161.8
	Minimum....	100.0	0.0	5.0	12.0	4.3	0.7	trace	61.8 43.7
1 yr.	Average.....	102.5	8.8	119.7	46.6	37.0	7.0	1.8	111.5
	Maximum...	104.0	13.8	171.0	60.5	64.8	15.5	3.3	194.0
	Minimum....	101.0	7.2 6.6	93.0 92.0	33.1 5.8	6.8 6.8	2.8	0.4	80.4 66.4
2 yrs.	Average.....	104.9	11.6	144.7	51.9	54.0	10.5	2.2	112.4
	Maximum...	109.0	16.7	199.0	75.6	75.1	18.7	5.7	214.0
	Minimum....	100.0	8.8 8.6	121.0 94.0	44.3 11.0	41.5 31.2	5.4	0.7	83.4 82.2
3 yrs.	Average.....	107.7	13.2	171.4	62.7	61.5	12.5	1.5	112.7
	Maximum..	112.0	18.3	224.0	81.8	79.8	20.8	6.1	202.0
	Minimum....	104.0	11.4 10.1	145.0 119.0	52.3 16.4	47.6 34.3	6.5	0.7	79.0 60.0
4 yrs.	Average.....	111.2	14.0	185.0	65.9	69.3	13.9	2.8	125.1
	Maximum...	118.0	18.9	238.0	83.8	89.1	22.1	6.7	203.5
	Minimum....	105.0	11.6 11.3	156.0 153.0	58.6 17.3	57.7 36.3	6.4	0.7	83.8 67.8
5 yrs.	Average.....	113.8	15.9	206.5	67.6	75.0	15.0	3.2	128.1
	Maximum...	125.0	19.2	251.0	92.6	105.5	22.4	7.7	254.2
	Minimum....	108.0	13.2 11.8	170.0 168.0	59.4 19.0	60.5 37.0	6.6	1.4	86.8 78.5
6 yrs.	Average.....	118.0	17.0	223.1	72.4	80.4	14.6	3.3	145.5
	Maximum...	132.0	21.2	284.0	95.8	109.0	22.3	8.3	245.3
	Minimum....	110.0	13.7 12.4	193.0 176.0	67.1 24.3	64.0 39.1	7.3	0.7	99.2 80.0
7 yrs.	Average	121.4	18.0	242.2	76.7	84.2	15.5	3.2	145.2
	Maximum...	141.0	22.7	306.0	100.0	114.9	25.2	8.5	264.5
	Minimum....	111.0	14.6 13.1	195.0 194.0	60.9 24.7	64.6 41.8	7.5	0.8	99.2 86.2
8 yrs.	Average.....	123.8	18.6	256.0	82.9	89.1	16.0	3.4	154.2
	Maximum...	132.0	24.2	339.0	112.0	126.6	26.5	9.2	280.3
	Minimum....	112.0	13.8 13.7	214.0 200.0	73.7 31.7	68.4 40.9	7.9	0.8	109.0 107.1

The minima, however, are of considerable interest, not so much for color and solids as for the acids and esters. Taking the acids for instance, the minimum for each year is given by one package, No. 2623, which is abnormal in many ways, and omitting it from consideration the minimum

of acids for the first year would be 33.1, only slightly below the average; for the second year it would be 44.3, and so on.

In order to show this and to eliminate the abnormal, the next to the lowest figures for the color, solids, acids, esters, and fusel oils are also included in the table.

TABLE XIVa.—AVERAGE, MAXIMA AND MINIMA DATA FOR BOURBON WHISKIES.

Calculated to 100 proof.

Age.	Data.	Proof.	Color.	Solids.	Acids.	Esters.	Aldehydes.	Furfural.	Fusel oil.
New	Average....	101.1	0.0	26.5	10.0	18.4	3.2	0.7	100.9
	Maximum .	104.0	0.0	161.0	29.1	53.2	7.9	2.0	171.3
	Minimum ..	100.0	0.0	4.0	12.0	13.0	1.0	trace	*71.3* 42.0
1 yr.	Average ...	101.8	7.1	99.6	41.1	28.6	5.8	1.6	110.1
	Maximum ..	103.0	10.9	193.0	55.3	55.9	8.6	7.9	173.4
	Minimum...	100.0	*5.4* 4.6	61.0 54.0	24.7 7.2	*17.2* 10.4	2.7	trace	*58.0* 42.8
2 yrs.	Average....	102.2	8.6	126.8	45.6	40.0	8.4	1.6	108.9
	Maximum ..	104.0	11.8	214.0	61.7	59.8	12.0	9.1	197.1
	Minimum...	100.0	6.9 5.7	81.0 78.0	*25.5* 23.3	*24.4* 11.2	5.9	0.4	*86.2* 42.8
3 yrs.	Average....	103.0	10.0	149.3	54.3	48.1	10.5	1.7	112.4
	Maximum ..	106.0	13.8	245.0	64.8	73.0	22.1	9.5	221.8
	Minimum...	100.0	8.9 7.0	*95.0* 90.0	38.4 32.1	*27.2* 12.1	5.9	0.6	*88.0* 43.5
4 yrs.	Average....	104.3	10.8	151.9	58.4	53.5	11.0	1.9	123.9
	Maximum ..	108.0	14.8	249.0	73.0	80.6	22.2	9.6	237.1
	Minimum...	100.0	8.6 7.4	101.0 92.0	40.4 40.4	*28.2* 13.8	6.9	0.8	*95.0* 43.5
5 yrs.	Average....	106.1	12.3	173.3	56.3	55.9	11.4	1.9	125.3
	Maximum ..	113.0	16.7	280.0	78.9	87.2	23.1	9.6	243.4
	Minimum...	101.0	11.8 8.4	*125.0* 114.0	*48.2* 42.7	*27.7* 17.3	7.1	0.8	*98.0* 45.1
6yrs.	Average....	107.9	13.1	185.1	67.1	64.0	11.9	1.8	135.3
	Maximum ..	116.0	17.5	287.0	81.0	83.9	23.3	9.5	240.0
	Minimum...	102.0	12.0 9.8	132.0 127.0	53.6 45.0	*36.4* 17.9	7.7	0.9	*98.1* 44.6
7 yrs.	Average....	109.6	13.9	200.9	71.9	63.3	12.4	1.9	137.2
	Maximum ..	120.0	19.4	309.0	86.4	90.0	26.7	8.3	243.4
	Minimum...	103.0	11.8 10.1	*140.0* 134.0	*60.6* 49.0	*37.1* 21.3	7.7	0.9	*98.2* 46.6
8 yrs.	Average....	111.1	14.2	210.3	76.4	65.6	12.9	2.1	143.5
	Maximum ..	124.0	20.9	326.0	91.4	93.6	28.8	10.0	241.8
	Minimum...	102.0	12.3 10.5	*152.0* 141.0	*64.1* 53.7	37.7 22.1	8.7	1.0	*110.0* 47.6

The point is especially noticable in the esters, for, omitting the minima, the lowest ester found on a four-year old whiskey was 57.7 grams, which is only slightly below the average, and would indicate that one might

expect in a four-year old rye whiskey 50 to 60 grams of esters to 100 liters.

Table XIV shows the average, maxima and minima data for the Bourbon whiskies.

The same may be said of this table as of the previous one in regard to the value of the maxima and minima figures.

All of these results indicate that we should expect lower figures with Bourbon whiskies than with rye.

The high solids shown in the maximum for the new spirit was due largely to ash, this being sample 2689, and the high ash changes, in this particular sample, the ratio between the color and solids.

TABLE XV.—AVERAGE DATA FOR ALL SAMPLES AND FOR RYE AND BOURBONS SEPARATELY.

Calculated to original volume.

Age.	Original volume.	Color.	Solids.	Acids.	Esters.	Aldehydes.	Furfural.	Fusel oil.
New	Whole.....	....	20.0	6.4	15.0	4.03	0.71	96.8
	Rye.....	....	13.6	4.7	13.7	4.91	0.97	83.2
	Bourbon.....	....	26.0	7.7	17.2	3.26	0.44	108.6
1 yr.	Whole.....	7.3	101.5	37.8	29.9	7.08	1.5	106.2
	Rye.....	8.4	114.6	41.8	35.3	8.71	1.7	106.8
	Bourbon.....	6.4	90.1	34.4	24.9	5.55	1.3	105.8
2 yrs.	Whole.....	8.6	124.2	46.1	42.9	8.34	1.7	108.1
	Rye.....	10.6	133.6	49.8	49.3	9.02	1.9	109.7
	Bourbon.....	6.7	114.8	42.7	37.3	7.78	1.4	107.3
3 yrs.	Whole.....	10.2	140.2	51.1	48.4	9.47	1.8	106.3
	Rye.....	11.5	150.4	54.4	54.3	9.80	2.2	104.4
	Bourbon.....	8.3	130.7	47.8	42.5	9.15	1.5	107.3
4 yrs.	Whole.....	10.2	140.4	51.6	50.9	10.2	1.9	104.3
	Rye.....	11.6	153.1	54.2	57.2	11.2	2.2	102.0
	Bourbon.....	8.9	127.7	48.9	45.0	9.3	1.5	106.3
5 yrs.	Whole.....	11.1	149.2	52.2	51.1	10.2	1.9	100.4
	Rye.....	12.2	158.8	54.8	57.5	11.3	2.5	100.1
	Bourbon.....	10.0	140.2	49.8	45.0	9.2	1.5	100.7
6 yrs.	Whole.....	11.1	151.4	53.2	50.7	10.2	1.9	104.7
	Rye.....	12.3	161.0	54.8	55.5	11.3	2.4	105.9
	Bourbon.....	10.1	142.5	51.8	45.2	9.1	1.4	103.8
7 yrs.	Whole.....	11.1	154.0	52.2	51.1	9.8	1.8	99.9
	Rye.....	12.0	161.3	51.9	56.6	10.6	2.2	98.8
	Bourbon.....	10.2	147.1	52.4	46.4	9.0	1.4	101.6
8 yrs.	Whole.....	10.5	155.2	53.1	50.9	9.6	1.8	98.0
	Rye.....	11.1	163.8	52.6	56.7	10.6	2.2	99.0
	Bourbon.....	10.0	147.7	53.6	45.9	8.8	1.5	97.1

This table gives the average of all the whiskies and the average of the rye and Bourbon separately, calculated back to the original volume, in order to eliminate the effects due to the concentration taking place while the spirit was stored. The more important points brought out by this table are brought out in the various charts. These figures show

more nearly the actual changes taking place, and prove that after the third year there is very little change in the amounts of the various substances present. As has been said before, the changes taking place in the whiskey after the third or fourth year are almost entirely due to the concentration which occurs.

These figures also show that the difference between rye and Bourbon whiskies holds good even when the results are corrected for loss of volume, proving that with the rye whiskies there has been a greater activity in the aging processes.

The fact that after the third year, the acids, esters, and aldehydes do not show any appreciable increase when corrected for loss in volume, does not necessarily mean that there is no formation of these substances in the barrel, as there may be some loss of them through the wooden walls of the barrel, with the alcohol and water which is constantly passing off; but the fact that they remain so constant in amount would indicate that these substances are left behind, in the same manner as the fusel oil and solids, by what might be called the selective action of the wooden membrane constituting the walls of the porous cell in which these products are stored.

Chart I shows the average of the changes taking place in the proof and the volume.

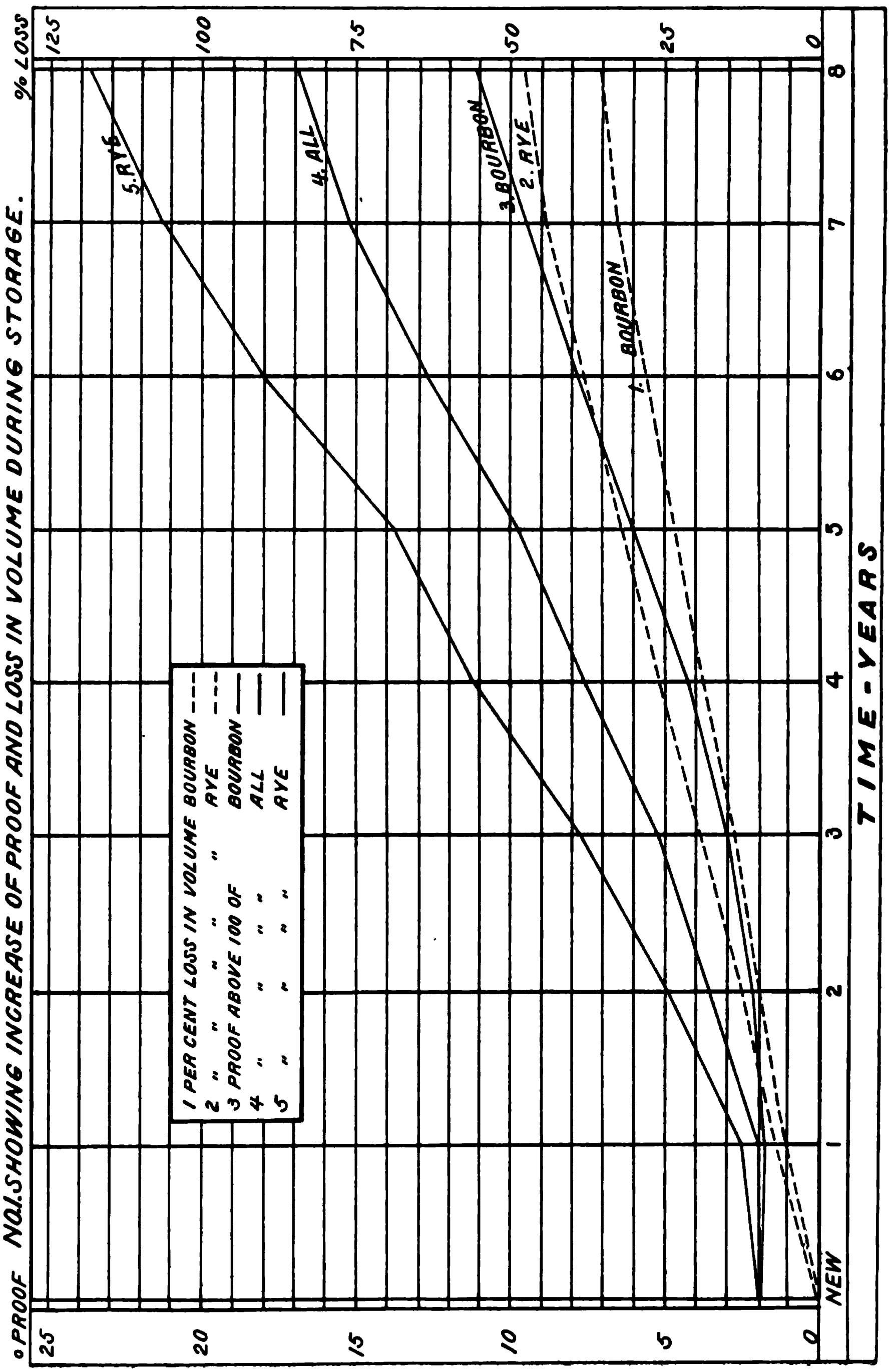
The proof increases, starting from approximately 100 proof, so that all that is shown on the curve are the degrees above 100 proof.

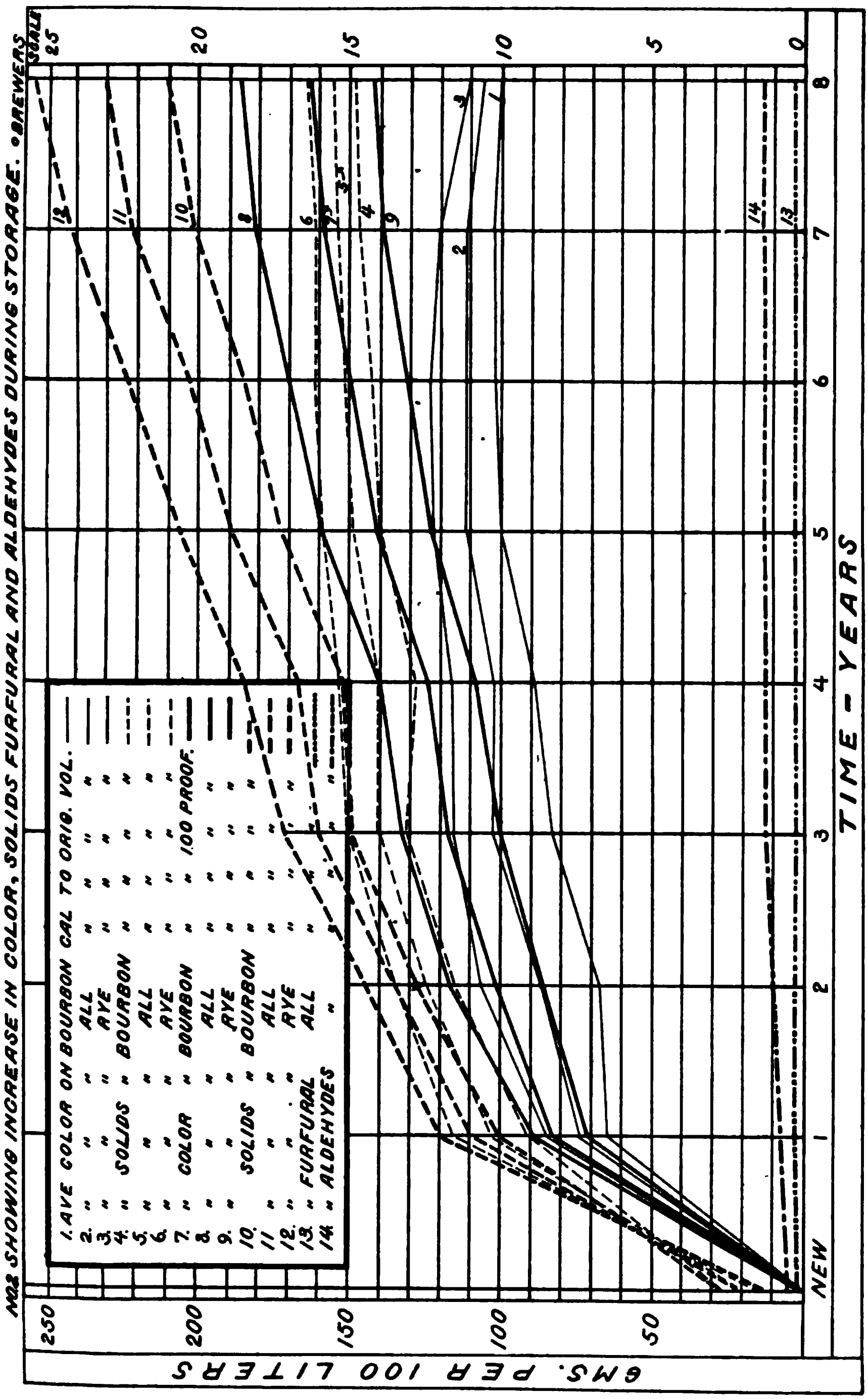
The changes in volume are plotted from the per cent. of loss in volume. The changes in proof and volume are important in their bearing on the changes that take place in the other substances.

The wide difference in rate of increase of proof shown by the rye and Bourbon whiskies is typical of the differences between them, and apparently has a simple explanation. In the case of the rye whiskies nearly all were aged in heated warehouses where the changes taking place are aided by the higher temperature. There is also a large loss of volume in the rye whiskies. as is shown by the lines. In short, there is much greater chemical activity, and so, greater changes. The amounts of acids and esters formed apparently have a direct relationship to the amount of the whiskey which passes through the wood of the barrel.

The Bourbon whiskies, on the other hand, are as a rule stored in unheated warehouses, so that there is less loss of volume in the spirit, and less increase in proof, and smaller amounts of acids and esters are formed. As a matter of fact, a much lighter bodied whiskey is formed, and from these results it would seem to be due to a greater extent to the method of storage than to the inherent differences in the whiskies themselves.

Chart II shows changes in solids and coloring matter, and the same differences between the rye and Bourbon whiskies as were noted on Chart


NO. SHOWING INCREASE OF PROOF AND LOSS IN VOLUME DURING STORAGE.
% PROOF
% LOSS
TIME - YEARS
NEW
1
2
3
4
5
6
7
8
0
5
10
15
20
25
0
25
50
75
100
125
1. BOURBON
2. RYE
3. BOURBON
4. ALL
5. RYE
1 PER CENT LOSS IN VOLUME BOURBON
2 " " " RYE
3 PROOF ABOVE 100 OF BOURBON
4 " " " ALL
5 " " " RYE


MAP SHOWING INCREASE IN COLOR, SOLIDS FURFURAL AND ALDEHYDES DURING STORAGE. • BREWERS SCALE
1. AVE COLOR ON BOURBON CAL TO ORIG. VOL.
2. " " ALL " " " "
3. " " RYE " " " "
4. " SOLIDS " BOURBON " " " "
5. " " ALL " " " "
6. " " RYE " " " "
7. " COLOR " BOURBON " " " " 100 PROOF.
8. " " ALL " " " "
9. " " RYE " " " "
10. SOLIDS " BOURBON " " " "
11. " " ALL " " " "
12. " " RYE " " " "
13. " FURFURAL ALL " " " "
14. " ALDEHYDES " " " "
GMS. PER 100 LITERS
250
200
150
100
50
0
5
10
15
20
25
NEW
1
2
3
4
5
6
7
8
TIME - YEARS

I are seen, namely, a marked increase during the first year, and a regular increase thereafter.

A comparison of the solids as calculated to 100 proof, and as calculated to the original volume, shows that the increase in the former is almost entirely due after the third year to the concentration taking place, the actual amount of solid matter in solution in any single barrel remaining practically the same after the third year. The same is true of the coloring matter and apparently little material is extracted from the wood after that time.

The remarkable similarity of the solids and color curves shows that there is a very close relationship between them. In fact, the relationship is so close that from the determination of the solids one could very closely calculate what the color should be, or from the color calculate the solids.

This relationship is of great value in the detection of the artificial coloring of whiskey, and in judging whether the solids are normal.

Chart III shows first the changes in fusel oil, calculated to 100 proof, and to the original volume. A gradual increase of fusel oil is shown as the whiskey ages, but it will be seen from the curve plotted from the calculations to the original volume that this change is due to concentration. The actual amount of fusel oil in a barrel of whiskey remains the same during the period of storage, but the whiskey itself shows a percentage increase.

These results, however, do not prove whether the fusel oils undergo change in aging, or whether any of the fragrant esters present are due to the fusel oils, because the method of analysis employed, first saponifies all of the esters and determines only the higher alcohols. The question as to the change taking place in the fusel oils must be answered by fractionating large quantities of a new and of a mature spirit and studying the composition of the higher boiling-point portions.

This chart also shows the changes occurring in the acids and esters, and further emphasizes the fact of the differences between rye and Bourbon whiskies. In every way the rye whiskies are the stronger, if one may use the term; that is, they contain more solids, color, acids, esters, etc., but all of these differences can be traced to the method of aging.

A very striking point which is also brought out by this chart is the change in relationship between the acids and esters in young spirits and the constant relation in matured spirits.

The average of the acids in the new spirit is 6 grams per 100 liters, and the esters average 16. In the spirit one year old this relation has changed, the acid being 44 grams against 33 grams for the esters. The second year the acids are 49, and the esters 47. The third year the acids are 59, and the esters 55. The fourth year the acids are 62 and the es-

ters 61, and they remain practically the same during the next four years. This shows that these two substances gradually approach an equilibrium, which they reach about the fourth year, and which does not change afterwards.

This point will be more fully discussed under chart V, showing the relationship of the acids and esters for a number of years.

NO. 4. RELATIONSHIP DEVELOPED ON STORAGE IN 4 YEAR OLD GOODS.

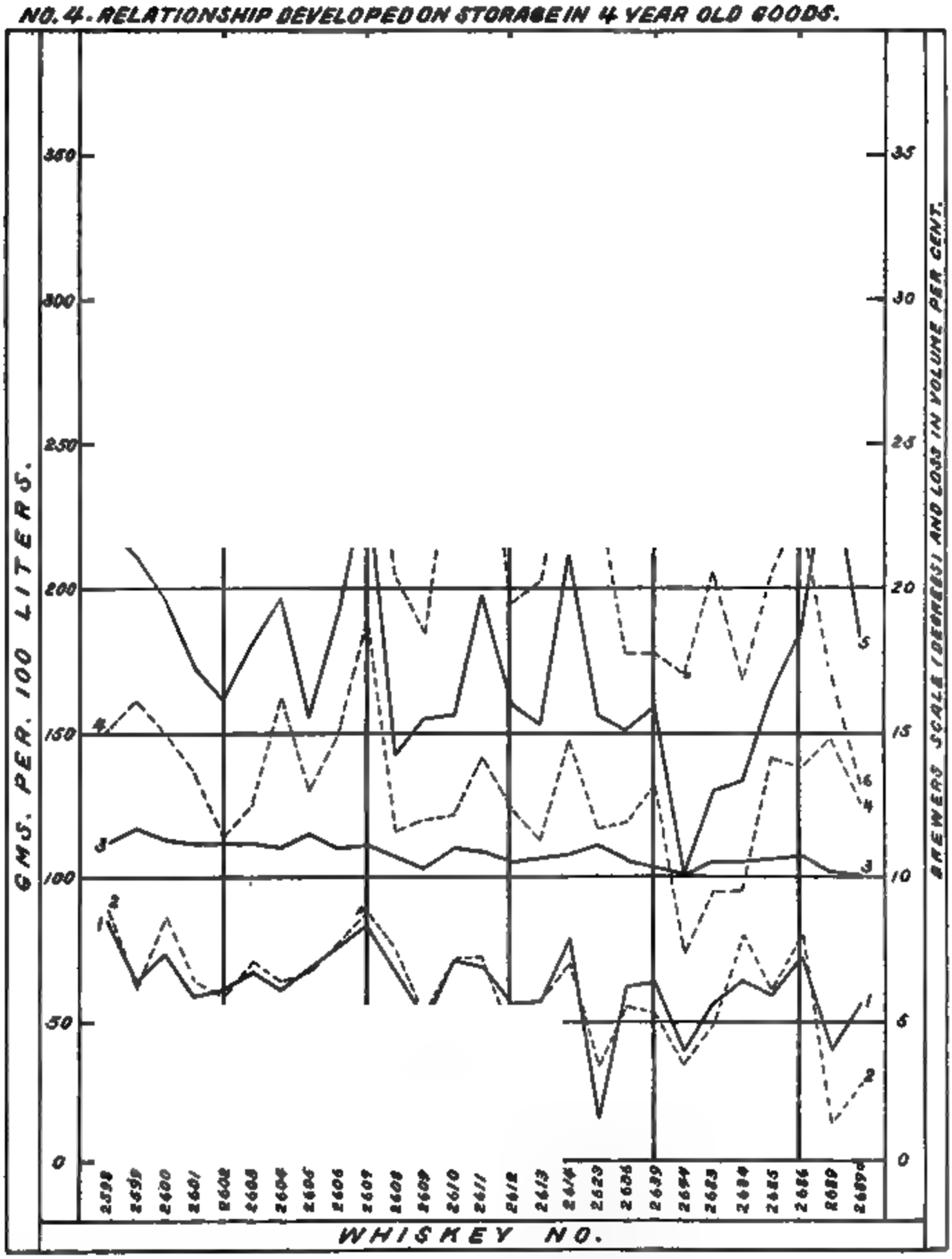


Chart IV, plotted from the results obtained on the four-year samples, shows the relationship of the various products present to each other and to the change in volume and the increase in proof.

Perhaps the most striking point brought out is the close relationship between the acids and the esters, the two lines following the same course across the sheet in the most remarkable way. But when we consider

the dependence of one on the other this is not so strange. It is apparent from this, as well as from Chart I, giving the averages, and from Chart V, on which are plotted the acids and esters, that these two substances reach an equilibrium, at the end of three or four years, as previously stated, which relationship does not change during longer storage. The meaning of this point will be discussed later.

This chart also gives the maxima and minima found for these samples, and in many cases shows how they may be explained by the loss in volume and increase in proof.

It also calls our attention to the fact that whereas when a whiskey has been matured in wood, and has a low acid content, we should expect to find a small amount of esters, it is shown in the new spirit and that when a year old this relationship does not hold, the two substances not having yet reached an equilibrium. This point may be of value in detecting young whiskies.

The color, solids, and concentration lines show a very close relationship, as might be expected, as they are dependent one on the other.

A study of all the lines reveals a marked relation among them. A high color, high solids, and high concentration are generally accompanied by high acids and esters, and low color and solids go with low acids and esters, which is a fact that will be of value in judging the purity of whiskies found on the market.

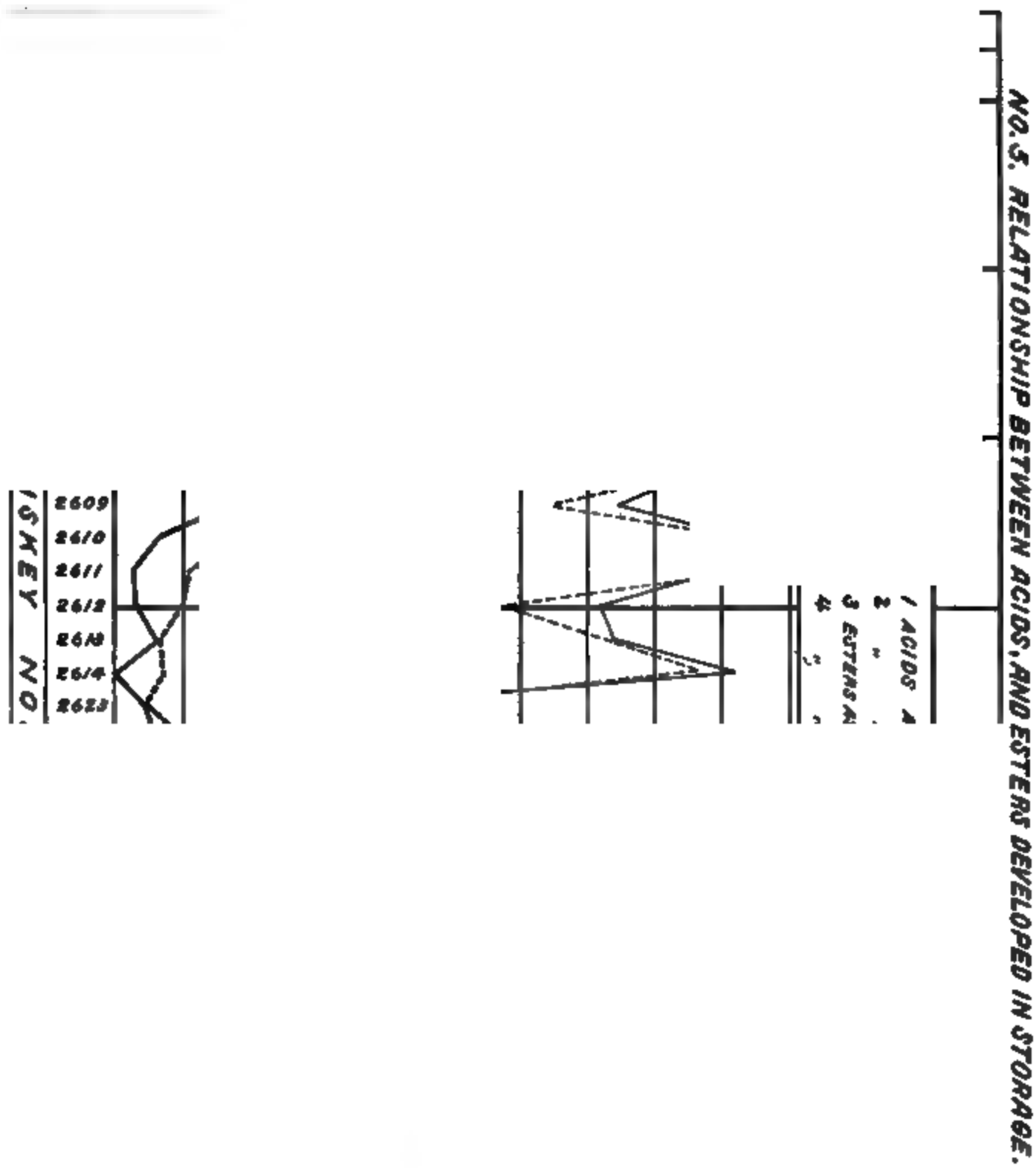
In fact, a study of the relationships found in these whiskies will be of great value in the determination of the adulteration of commercial whiskies. The range of variation that may take place in whiskies stored under different conditions is also shown by this chart.

Chart V shows the changes taking place in the acids and esters, using the results obtained on the new spirits, and those one, two and eight years old.

The great irregularity in the amounts of these substances in the new spirit, and the seeming lack of any relation, are at once noted; the acids, however, in every case, are lower than the esters, but at the end of the first year this has changed to a great degree, only seven samples showing higher esters than acids. The average of the esters, as shown in Chart III, is 9 grams per 100 liters below that of the acids.

At the end of the second year the esters are on the average 7 grams below the acids, and by the end of the fourth year the acids and esters average the same, retaining this relation up to the eighth year, when the experiment ceased.

This shows that in the aging process the acids are formed more rapidly at first than the esters, but later the esters form more rapidly, so that by the end of the fourth year they are present in about the same amounts, and remain the same during storage. The fact that this equilibrium is



reached at the end of three or four years indicates that there is some very close relation between the equilibrium of the acids and esters and the ripening of the whiskey. This is, of course, only one of the factors in the aging, but it seems probable that, when this condition of equilibrium is reached, the whiskey is matured in so far as the acids and esters contribute to that condition.

The chart also calls attention to some very abnormal samples, for instance, Nos. 2623 and 2689, both of which were aged in very cool warehouses, which fact probably explains in a degree the cause of their abnormalities.

Effect of Aging in Charred and Uncharred Packages.

In order to determine the effects of the material extracted from the barrel in the process of aging on the flavor of the whiskey, especially the difference between charred and uncharred packages, two samples of sour mash Bourbon whiskey, which had been produced by the same distiller from very similar mashes, as shown by the table below, and distilled in the same general type of still, were taken for comparison.

Composition of mash.	Whisky in uncharred package. Pounds.	Per cent.	Whisky in charred package. Pounds.	Per cent.
Malt	6048	10.9	4144	11.0
Rye	4704	8.5	2688	7.4
Corn	45024	80.6	30800	81.6

The samples had both been stored the same length of time in a warehouse and practically the only difference in the two products was in the kind of packages in which they were stored. The flavor, however, of the two whiskies was entirely different: the whiskey stored in the uncharred package lacked almost entirely the flavor so characteristic of American whiskies, having more of the flavor of Scotch or Irish whiskey, but without, of course, the smoky flavor of the Scotch, and was considered a very good-flavored whiskey by several persons who had a taste for such whiskies; the whiskey aged in the charred wood had the strong aromatic flavor which is so characteristic. In fact, the products are entirely different types of whiskey, showing that the method of aging is the important factor.

A study of the analytical data obtained, given in the following table, shows that there is a remarkable similarity in the amount of esters and acids and fusel oils in the two samples at the same age.

Serial number.	Proof.	Color in ½".	Color insoluble in H_2O. Per cent.	Grams per 100 liters. Solids. Per cent.	Acids. Per cent.	Esters. Per cent.	Aldehydes. Per cent.	Furfural. Per cent.	Fusel oil. Per cent.
2627, uncharred, 4th year	104.0	4.5	..	96.0	58.8	66.0	8.0	1.2	101.0
2635, charred, 4th year..	105.0	9.0	..	155.0	63.6	48.4	10.0	0.8	99.0
2627, uncharred, 8th year	110.9	7.0	23	160.0	81.6	84.5	10.8	1.5	112.0
2635, charred, 8th year..	110.0	13.5	61	181.0	81.6	65.6	13.2	1.2	125.0

The main difference between the two samples is in the amount of color and solids, and the composition of these solids and color, as shown by their solubility in water. The solids and color in the whiskey from the uncharred package are very much more soluble in water, being less of the resinous nature shown in the solids from the charred package, and in this respect it is very much like the Scotch whiskies which are aged in uncharred wood.

The resinous or oily nature of the solids in the whiskey from the charred

package is also shown in the whiskey itself, the foam being much more oily and remaining much longer than the foam on the whiskey from the uncharred package.

The actual amount of solids in the eight-year old goods is not so very different in the two samples, but the amount of color in the uncharred is only 7.0, as against 13.5 in the charred, and only 23 per cent. of the color in the uncharred is insoluble in water, while 61 per cent. of the color in the charred is insoluble, showing a wide difference in composition. As stated before, the whiskies are remarkably similar as far as the acids, esters, aldehydes, furfural and fusel oil are concerned, and the chief difference is in extractive matter.

The esters and acids in both have reached their equilibrium, and the maturity of the two samples, as far as these constituents are concerned, has been attained, but the marked difference in the flavor is due, without question, to the matter extracted from the barrels.

In order to determine the flavor due to the extractive matters, 100 cc. of each sample were taken and evaporated to 5 cc., so that as much as possible of the esters and aldehydes and other volatile substances would be driven off.

To this residue were added a few cubic centimeters of water. The odor of the residue from the charred package was very strong, having the peculiar aroma of American whiskey. The taste of this residue was also very strong, being both resinous and astringent, and there can be no doubt that these materials, which are left in the residue, make up, to a great extent, the peculiar aroma of American whiskey, as distinguished from Irish or Scotch whiskey.

The residue from the uncharred package has a somewhat similar odor, and a slightly sour, astringent taste, entirely different from that of the charred package. This great difference in the flavor and odor of the residues from charred and uncharred packages is to a great degree the difference in the flavor and odor of the matured whiskey.

Whether all of these solids come from the package has not been proved, as part of these solids may come from the oxidation of some of the volatile oils which are distilled over, rendering them non-volatile, but a sample containing only traces of fusel oil, which had been produced with a rectifying still by which practically all of these oils are removed, and which had been aged in charred wood, was examined, and the solids prepared as above, had practically the same flavor. This at least indicates that the peculiar flavor which characterizes American whiskies, as compared with Scotch and Irish whiskies, is largely due to the kind of package in which they are aged.

It cannot be considered, however, that the acids, esters, and other ingredients do not enter into the flavor of the matured product, but the

peculiar flavor of American whiskies which distinguishes them from other whiskies is undoubtedly derived from the extractive matter from the charred wood in which they are stored while aging.

This fact is brought out by sample 2612, which was alcohol aged in wood, and lacked the taste of the whiskies produced in other type of stills, in which little rectification takes place.

Flavor.

It must be remembered that the flavor of these whiskies was determined at the same time, when all were of the same age, about nine years—the new spirit having been this length of time in bottle—and when we consider that it still had the odor of new whiskey, and showed no development of acids and esters, but was still raw spirit, it seems proved that none of the maturing processes take place in glass, and that whiskey after it is bottled will not improve.

In fact, none of the changes that take place in the wood occur in the bottled sample. Take, for instance, the year-old samples which have a very considerable amount of color and solids, and yet do not, in the eight years in which they are in glass, change as to solubility, like the solids and color of whiskey kept in wood. In fact in no way was any change indicated in the samples in glass.

No effort was made to judge when a certain whiskey had matured. The only comparison made was of the new spirit, the spirit four years in wood, and that eight years in wood, and then only in a general way to see whether the four- and eight-year old goods could be considered good whiskies, and whether the new spirit could in any way be said to have improved. In no case could the new spirit be said to be anything but raw spirits with the new whiskey flavor, not to be compared with the spirit one-year old.

The judging of the flavor and taste of the whiskies was done by a special gauger of the Bureau of Internal Revenue, who had a long experience in deciding between straight whiskies and compound whiskies, and has shown his ability to detect the difference. The samples were submitted without name for an unprejudiced decision. The results will not be given in detail, as all of the matured samples would doubtless be considered good whiskey, and a judgment as to quality is very difficult and unsatisfactory, and unnecessary for this paper.

Special attention was given to a few samples which were peculiar: No. 2612, which was practically cologne spirits aged in wood, No. 2623, which was abnormal in content of acids and esters, No. 2689, which was abnormal in content of esters, and Nos. 2625 and 2627, which were stored in uncharred packages.

The judgment of No. 2612 was that it had the peculiar aroma of Amer-

ican whiskey, but had the taste of spirits, and little difference could be noted between the two-year old sample and the eight-year old.

The judgment of No. 2623 was that it was a good flavored whiskey, but with very light body.

No. 2689 was pronounced a good flavored whiskey.

Nos. 2625 and 2627, the samples aged in uncharred packages, were both called immature whiskey, even when the eight-year old sample was tested. But this judgment was based on a comparison with those aged in charred packages.

On that basis the eight-year old sample was thought to be about 1 to 2 years old. This shows what a marked effect the storage in charred wood has upon the flavor of the whiskey.

Conclusions.

1. There are important relationships among the acids, esters, color, and solids in a properly aged whiskey, which will differentiate it from artificial mixtures and from young spirit.

2. All of the constituents are undergoing changes as the aging process proceeds, and it is evident that the matured whiskey is the result of these combined changes.

3. The amount of higher alcohols increases in the matured whiskey only in proportion to the concentration.

4. Acids and esters reach an equilibrium, which is maintained after about three or four years.

5. The characteristic aroma of American whiskey is derived almost entirely from the charred package in which it is aged.

6. The rye whiskies show a higher content of solids, acids, esters, etc., than do the Bourbon whiskies, but this is explained by the fact that heated warehouses are almost universally used for the maturing of rye whiskies, and unheated warehouses for the maturing of Bourbon whiskies.

7. The improvement in flavor of whiskies in charred packages after the fourth year is due largely to concentration.

8. The oily appearance of a matured whiskey is due to material extracted from the charred package, as this appearance is almost lacking in whiskies aged in uncharred wood.

9. The "body" of a whiskey, so-called, is due largely to the solids extracted from the wood.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

THE CONDENSATION OF CHLORAL WITH PRIMARY AROMATIC AMINES. II.

BY ALVIN S. WHEELER.

Received October 21, 1907.

A number of condensation products of chloral with primary aromatic

amines have already been described. The first mention of such a reaction is probably that of Maumené,[1] who hoped to obtain indigotin by the action of chloral (2 mols.) upon aniline (3 mols.). His product was a brownish black uncrystallizable substance containing no chlorine. Schiff and Amato[2] first described a condensation product of chloral (1 mol.) and aniline (2 mols.) with the formula $CCl_3CH(NHC_6H_5)_2$. In the same year Wallach[3] described this compound. Later,[4] he gave a full description of the products obtained from aniline, *p*-toluidine, and a sample of xylidine boiling at 212–216°. Eibner[5] studied the condensation of chloral with *p*-nitraniline, *m*-chloraniline, *p*-chloraniline, and 1,2,4-dichloraniline and showed that 1,2,4,6-trichloraniline and 2,6-dichlor-4-nitraniline do not react. Wheeler and Weller[6] prepared the *o*- and *m*-nitraniline compounds and Wheeler and Daniels[7] showed that only addition products could be obtained with the naphthylamines. Niementowski and Orzechowski[8] found that one molecule of chloral condensed with one molecule of anthranilic acid but later[9] obtained the expected diphenamine compound. Finally Rügheimer[10] describes the compounds with *o*- and *p*-phenylenediamine and 1,2,4- and 1,3,4-toluylenediamine. He also states that only addition products are obtained with the naphthylamines.

The chloral diphenamine compounds vary considerably in stability. Most of them may be kept for years. They possess great crystallizing power. Their behavior toward alkalies is variable. The aniline derivative is decomposed by alcoholic potash into aniline, chloroform and phenyl cyanide according to Wallach. The *p*-nitraniline derivative, on the other hand, is converted into a hydroxy compound, one chlorine atom being replaced by a hydroxyl group according to Wheeler and Glenn.[11] They are not stable in the presence of strong mineral acids, which split them so as to re-form the amine. Eibner has shown that boiling acetic anhydride and benzoyl chloride give the acetyl or benzoyl derivative of the original amine. Finally, the writer has found that all of them react with great readiness with bromine in the cold. There is a substitution of one hydrogen atom in those which have been analyzed. This substitution probably occurs in the methylene group of the chloral residue.

[1] Ber., 3, 246 (1870).
[2] Gazz. chim. ital., 1, 376 (1871).
[3] Ber., 4, 668.
[4] Ann., 173, 274.
[5] *Ibid.*, 302, 335.
[6] This Journal, 24, 1063.
[7] J. Elisha Mitchell Sci. Soc., 22, 90 (1906).
[8] Ber., 28, 2812.
[9] *Ibid.*, 35, 3898.
[10] *Ibid.*, 39, 1653.
[11] J. Elisha Mitchell Sci. Soc., 19, 63 (1903).

Chloral and p-*Bromaniline. Trichlorethylidenedi*-p-*bromphenamine*, $CCl_3CH(NHBrC_6H_4)_2$. With C. W. MILLER.—Ten grams of *p*-bromaniline were dissolved in 50 cc. benzene and 8 grams chloral (4.2 grams required by theory) in 10 cc. benzene were added. The mixture was concentrated one-half on the water bath and cooled. A white flocculent precipitate came down, giving a melting-point of 135°. On further evaporation a second and much larger crop was obtained, showing a melting-point of 119°. By several recrystallizations from benzene the melting-point was raised to 140°. The yield was very high. Analysis: calculated for $C_{14}H_{11}N_2Cl_3Br_2$, C 35.45, H 2.34, N 5.93, Cl + Br 56.24; found, C 35.03, H 2.46, N 6.38, Cl + Br 55.58.

Trichlorethylidenedi-*p*-bromphenamine consists of fine colorless needles, melting at 140° and decomposing at 205°. It is extremely soluble in alcohol, acetone, glacial acetic acid and hot benzene. It is sparingly soluble in cold benzene and insoluble in ligroin. It is readily purified by using a mixture of benzene and ligroin. It is not decomposed by boiling water but is split by boiling concentrated hydrochloric acid with the regeneration of *p*-bromaniline. A bromine derivative is easily obtained by adding bromine to a glacial acetic acid solution. The product, consisting of colorless plates, melts at 203° after several recrystallizations from glacial acetic acid. Determinations of carbon, hydrogen and nitrogen give very satisfactory figures for a monobrom compound. Chlorine gives a similar reaction. The product, crystallizing in long colorless needles, melts at 93° after recrystallization from glacial acetic acid. A study of the constitution of these halogen derivatives is under way.

Chloral and o-*Anisidine. Trichlorethylidenedi*-o-*methoxyphenamine*, $CCl_3CH(NHOCH_3C_6H_4)_2$. With W. S. DICKSON.—Two molecules (12.3 grams) of *o*-anisidine were dissolved in 50 cc. benzene and one molecule (7.3 grams) of chloral was added. After warming a short time on the steam bath a small quantity of colorless needles deposited. These decomposed at about 215° and weighed 0.95 gram. On concentration of the filtrate in a desiccator a mass of fern-like crystals was obtained mixed with a thick liquid. After filtering, the crystals were pressed on a porous tile. The product was white, melted at 112–114° and weighed 9.7 grams. On recrystallizing from benzene the melting-point was raised to 121°. The thick liquid finally solidified, considerably increasing the yield. Analysis: calculated for $C_{16}H_{17}O_2N_2Cl_3$, Cl 28.35, N 7.47; found, Cl 28.35, N 7.30.

Trichlorethylidenedi-*o*-methoxyphenamine crystallizes from ligroin or benzene in magnificent rhombohedra, one-half inch or more long, with a slight yellow color. It is easily soluble in cold benzene and carbon tetrachloride and in hot glacial acetic acid. It is slightly soluble in cold ligroin and fairly soluble in hot ligroin. It crystallizes from alcohol in long slender prisms. One hundred cc. of boiling alcohol will dissolve ap-

proximately 7 grams and at 25° about 2.5 grams. It is insoluble in and unchanged by boiling water. When boiled in concentrated hydrochloric acid the odor of chloral could be detected in the vapors. A bromine derivative is readily obtained by adding bromine to a concentrated glacial acetic acid solution. The product crystallizes in clusters of needles which decompose at about 230°. This compound is being further investigated.

Chloral and p-*Anisidine. Trichlorethylidenedi*-p-*methoxyphenamine*, $CCl_3CH(NHOCH_3C_6H_4)_2$.—To a solution of 12.3 grams of *p*-anisidine in 20 cc. of benzene (a nearly saturated solution) is added 7.3 grams of chloral. The solution turns to a dark red color at once, much heat is developed and a deposition of 0.22 gram of small colorless crystals occurs. These decompose at about 215° as in the case with *o*-anisidine. After filtering, the reaction mixture is boiled fifteen minutes and then allowed to stand several hours. An abundant crystalline precipitate formed. After filtering and pressing on a clay plate, the product melted at 115° and weighed 10.5 grams. A further yield was obtained from the mother-liquor. Purification by means of the mixed solvent, benzene and ligroin, raised the melting-point to 118–120°. Analysis: calculated for $C_{16}H_{17}O_2N_2Cl_3$, Cl 28.35; found, 28.41.

The *para* compound crystallizes from ligroin in brilliant scales, showing a strong pink color in the mass. It melts at 118–120° and decomposes at 158°. It is fairly soluble in cold benzene, alcohol and ether. It is readily soluble in glacial acetic acid, hot benzene and hot alcohol. The alcoholic solution emits a most disagreeable odor and on spontaneous evaporation to dryness a jet black crystalline mass remains. On treatment with bromine in glacial acetic acid solution a crystalline product is obtained which blackens at about 198°. This compound is being studied further.

Chloral and Anthranilic Acid.—The product obtained in this case depends upon the proportions used. One molecule of chloral will condense with one or two molecules of anthranilic acid with the elimination of one molecule of water. The two products have been described by Niementowski but his method yields a mixture and since we wish to prepare the compounds in order to study their bromine derivatives we have improved upon his method.[1]

Trichlorethylidene-o-*aminobenzoic Acid* (*Chloral-anthranilic Acid*), $CCl_3CH{:}NC_6H_4COOH$. With W. S. DICKSON.—Five grams of anthranilic acid were dissolved in 40 cc. of boiling benzene (a saturated solution) and 5.5 grams chloral in 10 cc. benzene were added. The weights are in the proportion of one molecule to one molecule. The mixture was boiled

[1] Since writing the above, larger quantities of the mono-compound have been prepared in benzene solution and a small amount of the di-compound has been isolated from the product.

under a reflux condenser for three hours, filtered from a small precipitate and cooled. A crystalline deposit, weighing 5 grams and melting at 148–151°, separated. The crystals were large elongated tables occurring in clusters. From the filtrate was obtained 3 grams of material, melting at 145–150°. Several recrystallizations from benzene raised the melting-point to 152°. Niementowski and Orzechowski[1] prepared this compound without the use of any solvent. They used an excess of chloral and got several by-products. We have tried their method but have employed theoretical proportions. Even so we get the same by-products. The mortar was placed in a block of ice and the previously cooled substances rapidly stirred together. The mixture liquefied and then rapidly became very hard. This product decomposed at about 127°, after two hours on ice at 124° and after three hours more at room temperature at 118°. It was then rubbed up with a little water and filtered. The decomposition point rose to 135°. Now, taking advantage of the marked difference in solubility in benzene of the mono- and di-compounds (not observed by Niementowski) the crystalline mass, weighing 8.2 grams, was extracted with 45 cc. boiling benzene. From the extract there separated a mass of colorless needles, weighing 3.7 grams and melting at 149–152°, consisting therefore of the nearly pure mono-compound. On evaporating the filtrate a residue was obtained, weighing 1.3 grams and melting at 160°, a fair quality of the di-compound. A second extraction was made with 35 cc. of boiling benzene. On cooling, this yielded a product weighing 0.8 gram and melting at 162° and a residue melting at 157° after evaporation. There still remained an insoluble residue, dark purple in color. These results are in marked contrast to those obtained by our method of boiling in benzene, for we get practically only the mono-compound and consequently a much larger yield. We further identified the mono-compound by a chlorine determination. Calculated for $C_9H_5O_2NCl_3$, Cl 39.92; found, Cl 39.43.

On treating a glacial acetic acid solution of this compound with bromine a bromo derivative is obtained in large quantity. On cooling a hot glacial acetic acid solution, it deposits in clusters of fern-like crystals which decompose at 237°. This compound is under investigation.

Trichlorethylidenedi-o-aminobenzoic Acid (*Chloral Di-anthranilic Acid*), $CCl_3CH(NHC_6H_4COOH)_2$.—Five grams (2 mols.) of anthranilic acid in 40 cc. boiling benzene were treated with 2.9 grams (1 mol.) of chloral in 10 cc. benzene and boiled under a reflux condenser for three hours. During the boiling there separated 3.25 grams of the di-compound, melting at 164–165°. On evaporation to dryness the residue was found to weigh 4.0 grams and to melt at 157°. The pure compound melts at 165°. The

[1] Ber., 28, 2812.

method of Niementowski[1] was tried and although found to be better than for the preparation of the mono-compound, it gave a smaller yield and a larger amount of unknown colored by-products. Analysis: calculated for $C_{16}H_{13}O_4N_2Cl_3$, N 6.96, Cl 26.11; found, N 6.76, Cl 26.10.

The di-compound consists of a crystalline powder and may be purified by precipitating its ether solution with ligroin. Upon boiling eight hours with acetic anhydride and cooling, a crystalline substance deposits, melting at 183° and crystallizing from benzene in needles. This corresponds to acetyl-*o*-aminobenzoic acid. On treating a glacial acetic acid solution with bromine, there is almost instantly obtained a heavy precipitate which after recrystallization from glacial acetic acid melts with decomposition at 236°. This behavior is surprisingly like that of the bromo derivative of the mono-compound.

Chloral and o-*Toluidine. Trichlorethylidenedi-*o-*tolamine*, $CCl_3CH(NHC_6H_4CH_3)_2$. With STROWD JORDAN.—Chloral and *o*-toluidine were brought together directly in the proportion of one molecule to two molecules. No advantage was found in using benzene as a solvent. To 28 grams *o*-toluidine 19.3 grams chloral were added; the mixture turned dark red and the temperature rose to 80°. After standing for some time, often over night, a quite hard crystalline cake formed. This was dissolved up in ether or successively extracted with benzene. In either case, a small residue weighing 0.7 gram remained. This was pale greenish in color and melted at 213°. The main product of the reaction was recrystallized from ether until the melting-point reached 80°. The yield was 70 per cent. of the theoretical. Analysis: calculated for $C_{16}H_{17}N_2Cl_3$, Cl 30.95; found, 30.77, 30.40, 30.96. The Stepanow method was employed in the secend and third analyses and found to be extremely convenient. With somo of our compounds we have found it impracticable on account of the deep color of the solution. We found it advisable to follow the suggestion of Rosanoff and Hill[2] and filter off the silver chloride before titrating.

Trichlorethylidenedi-*o*-tolamine crystallizes in very long silky needles. It is not very stable in solution or when exposed to the light. It is decomposed by water into chloral and *o*-toluidine. It is soluble in cold alcohol, ether, acetone, chloroform, carbon tetrachloride and glacial acetic acid, in hot ligroin and hot benzene. The pure substance melts at 80° and will melt repeatedly at that temperature. A bromine derivative is readily obtained in glacial acetic acid solution. This consists of colorless plates which melt with decomposition in the neighborhood of 268°.

Physiological Action.—The tolamine was found to have a physiological action by an accidental observation. Mr. Jordan unintentionally got a

[1] Ber., 35, 3898.
[2] This Journal, 29, 269.

small amount in his mouth and in about an hour a feeling of numbness spread over him to such a degree that pinching the flesh produced little sensation. Mr. Jordan was frightened by his condition but in an hour and a half he returned to a nearly normal state. The physiological action of this and other diphenamine compounds of chloral will be studied with care, some preliminary experiments on rabbits by Dr. MacNider, of this University, having confirmed the observation of such an action.

CHAPEL HILL, N. C.,
October 16, 1907.

NOTES.

The boiling point of isobutane, which is given in the literature, is based on a determination by Butlerow.[1] He found that the gas begins to condense to a liquid at —17°.

Some years ago Mabery[2] isolated from petroleum a hydrocarbon which boiled at 0° and which he considered to be isobutane on the basis of the chloride obtained from it, which boiled at 68–69° and which he considered to be isobutyl chloride. Since 2-chlor-2-methyl-propane boils at 67.3–67.8°[3] and has a specific gravity closely approaching that of Mabery's product, it seems probable that the chloride which he obtained was in reality a derivative of normal butane, and not of isobutane. This view is further supported by the work of Pelouze and Cahours,[4] who found that a chloride boiling at 65–70° is obtained by the action of chlorine on normal butane.

It seemed of interest to prepare isobutane again, and make a new determination of the boiling-point. This was done by Mr. E. F. Phillips under my direction in the laboratory of the Rose Polytechnic Institute several years ago, and the results were reported to Professor Mabery, thinking that he would, at some time, publish something further upon the subject. As he has not done this and informs me that he does not expect to take up the subject again, it seems proper to give the results of our experiments.

The isobutane was prepared by the reduction of isobutyl iodide with zinc and dilute alcohol. The gas was purified and dried by passing it through bulbs containing alcohol and also bulbs containing concentrated sulphuric acid. It was condensed to a liquid by a freezing mixture and the temperature at which the vapor of this liquid exerted a pressure of 760 mm. was determined. This temperature was found to be —11.5°. A considerable part of the liquid was allowed to evaporate and the deter-

[1] Ann., 144, 13.
[2] Am. Chem. J., 19, 247.
[3] Norris and Green, *Ibid.*, 26, 308.
[4] Jsb., 1863, 524.

mination repeated, proving that the liquid was practically homogeneous. A determination of the density of the gas also gave results agreeing satisfactorily with the theory.

There seems, therefore, to be little question that the butane obtained by Professor Mabery was in reality normal butane, and that the boiling-point of isobutane is —11.5°. W. A. NOYES.

The following note has been received from Prof. Mabery to whom this note was submitted in manuscript:

"I have no reason to doubt the accuracy of Professor Noyes' observation on the boiling-point of isobutane. It is not incompatible with our results on the butane in petroleum. I have intended to refer to this subject more fully in a later paper, a resumé of the composition of American petroleum." C. F. MABERY.

UNIVERSITY OF ILLINOIS,
URBANA, ILL.

The Stereochemistry of Indigo.—The last paragraph of this paper (This Journal, December number, 1907, p. 1743,) in which the structures of the two diacetyl indigo whites are discussed on the spatial hypothesis, assumes that both compounds possess the ketone structure. If both rearrange to the tautomeric enol forms, it should be pointed out that there would still be two stereoisomers (*cis* and *trans*) which it would not be possible to resolve into optically active isomers. K. GEORGE FALK AND J. M. NELSON.

REVIEW.

RESEARCHES ON THE DENSITY OF GASES

CARRIED ON DURING 1904, 1905 AND 1906 IN THE PHYSICAL CHEMISTRY LABORATORY OF THE UNIVERSITY OF GENEVA.[1]

BY PHILIPPE A. GUYE.

Received October 1, 1907.

The present article contains a résumé of the results obtained during the course of three years' work on the exact density of gases. The work has been carried on in collaboration with Messrs. Jaquerod, Pintza, Davila, Gazarian and Baume, and until now has been the subject of only isolated publication (Jaquerod and Pintza, *Compt. rend.*, **139**, 129 (1904), (SO_2 and O_2); Guye and Pintza, *Ibid.*, **139**, 679 (1904); **141**, 51 (1905), (N_2O, CO_2 and NH_3); Guye and Davila, *Ibid.*, **141**, 826 (1905), (NO); Guye and Gazarian, *Ibid.*, **143**, 1233 (1906), (HCl); Baume, unpublished (1907), (SO_2)). These have contributed to the problem of the physicochemical determination of exact molecular weights, with a view to checking up the

[1] From *Archives des Sciences Physiques et Naturelles*, **24**, 32–62. Translated by Helen Isham.

atomic weights. This problem has become one of great importance, and has been taken up by Leduc (Leduc: *Recherches sur les gaz*. Paris, Gauthier-Villars (in part), *Ann. Chim. Phys.* (1897)), Lord Rayleigh (Rayleigh, *Proc. Roy. Soc.*, **43**, 353 (1888), (H_2 and O_2); **50**, 449 (1892), (H_2 and O_2); **53**, 134 (1893), (O_2, H_2, N_2 atm. air); **55**, 340 (1894), (N_2); **59**, 198 (1896), (Ar, He); **62**, 204 (1897), (CO, CO_2, N_2O); **74**, 181 (1904), (N_2O); *Phil. Trans. Roy. Soc.* **204A**, 351 (1905); Rayleigh and Ramsay, *Phil. Trans. Roy. Soc.* **186A**, 187 (1895)), Morley, (*Z. physik. Chem.*, **20**, 1, (O_2); **22**, 2, (H_2), (1896)), Gray, (*J. Chem. Soc.*, **87**, 1601 (1905), (N_2; O_2, NO); *Proc. Chem. Soc.* (1907), (HCl)), as well as Perman and Davies (Perman and Davies; *Proc. Roy. Soc.* **78A**, 28 (1906)). Details of the methods, and the method of calculating the results, will be given under the head of generalities; next a review of the results obtained at Geneva compared with those of other experimenters, and finally a summary of those values which appear to the author to be most reliable.

I. Generalities.

Methods.—Two general methods have been used in density determinations, that of the balloon and that of the volumeter.

The balloon method, the details for which have been worked out by Regnault (weighing the balloon empty and filled with gas, against a counterpoise of the same volume, reducing to weight *in vacuo*, etc.) has been used in recent work, taking into account the correction for the contraction of the empty balloon, and the correction for the compressibility of the gas (deviation from the law of Mariotte between the existing pressure and that of 760 mm. Hg). The recent work is also characterized by a gradual reduction of the capacity of the balloon. Morley worked with balloons of from 8 to 21 liters capacity. Rayleigh used one of about 1.8 liters capacity, Leduc one of about 2.3 liters. The work in this laboratory has led to a still further reduction of the capacity of the balloon, and two balloons, destined to act as checks upon each other, one 0.8 liter, the other about 0.4 liter in capacity, filled at 0° and under the same pressure conditions, have been used.[1]

Perman and Davies have used a balloon of 0.5 liter capacity, while Gray has reached the lowest unit, and in the determination of nitric oxide used one of about 0.267 liter. Contrary to what one might expect, *a priori*, the determinations with the small balloons are at least as concordant, among themselves, as those with balloons of larger volume. The experiments with the two-liter balloons below, show, on the whole, a better agreement than those with balloons varying from 8 to 21 liters. This may be due either to the fact that the corrections for the original weights (for contraction, etc.) are smaller with the small balloons, or that the chances of accidental error, especially those due to the condition of the surface of the glass, are diminished.

The only objection which can be raised to the use of the small balloons is the possibility of the condensation of gas on the inner wall. If there were such condensation, the density of gases measured in small balloons should be greater than in the larger balloons, and this error should be especially great in the case of the hygroscopic gases, sulphur dioxide, ammonia, hydrochloric acid gas, etc.

[1] Experiments using still smaller balloons are being carried on at present.

The recent determinations show that while the capacity of the balloons varies to a great extent, the results obtained are very concordant, especially in the case of ammonia and sulphur dioxide.

By the volumeter method (capacity = about 1.8 liters) Perman and Davies found 0.77085 gram for the weight of a liter of ammonia gas under standard conditions, while by the balloon method they obtained 0.77086 gram for the same gas, using a balloon of 0.5 liter capacity. Guye and Pintza, using a volumeter of 3.5 liters capacity, found 0.7708. Thus there is no appreciable difference between the values obtained by the large and small balloons. Jaquerod and Pintza have obtained the value 2.9266 grams for the weight of 1 liter of sulphur dioxide, using a volumeter of 3.5 liters capacity; Leduc, using a 2.3 liters balloon, found 2.9266; and Baume has recently repeated this determination, using two balloons of 0.53 liter and 0.32 liter capacity, respectively, on gas prepared under the same conditions as that used by Jaquerod and Pintza, and has found 2.9266 grams.

The only necessary precaution consists in rinsing the balloon, not only with air dried over phosphorus pentoxide, but also several times with the well-dried gas, the density of which is to be determined, taking care that between each rinsing operation the vacuum in the balloon is as perfect as possible, and that air does not enter the balloon between each determination.

It might, nevertheless, be assumed that there is a slight condensation of the gas on the inner wall of the glass, similar to the moisture adhering to glass. The author's experience (in collaboration with Gazarian) on the density of hydrochloric acid gas, which is extremely hygroscopic, does not justify this assumption. In fact the balloons were at first rinsed only two or three times with dry hydrochloric acid gas. Under these conditions, with a balloon of 0.385 liter capacity, the values for the density showed a regular decrease, and did not become constant until after the fourth determination. Using a larger balloon (0.818 liter capacity) this point was not reached after the seventh filling. These facts led to the conclusion that after twelve successive rinsings[1] with the dry gas, each rinsing followed by a complete evacuation of the balloon, the condensation of the gas on the interior wall of the balloon is not sufficiently great to affect the results to an appreciable extent, provided air has not entered the balloon during the process of rinsing. (If Bunsen's observations are correct, the moisture given off by the glass at high temperatures is not due to condensation on the surface, but to water incorporated chemically or physically in the mass of the glass.)[2]

[1] In the case of non-hygroscopic gases 5 to 6 successive rinsings, each followed by complete evacuation, are sufficient.

[2] If we admit that the condensation of the gas on the interior surface of the balloon is not generally appreciable, still we do not claim that it is absolutely nil. In order to determine the condensation most accurately, two or more balloons of very different capacities should be filled at the same time, under the same conditions of pressure and with gas from the same source. The determinations of the densities of nitric oxide and sulphur dioxide, using two balloons filled simultaneously, furnish some preliminary information on this subject. The following averages have been

The *volumeter method*, used as an exact method for the first time by Morley in the determination of the density of hydrogen, has been used in two ways. According to the first method the gas is evolved from an apparatus which may be weighed, and constructed in such a fashion that the gas alone, in a state of perfect purity and dryness, escapes. The gas then passes through a tight-fitting joint into a system of one or more balloons of known capacity, maintained at 0°, and which have been evacuated by a mercury pump. The pressure is measured either with a special manometer, or simply by connecting the apparatus with the tube of a barometer. Morley employed the latter method in his fourth series of measurements of hydrogen, and it has also been employed at Geneva. Knowing then the temperature and the pressure, the capacity of the balloons and the loss of weight of the generating apparatus, the density may be calculated.

According to the second method the volumeter, previously evacuated, is filled with the pure gas. The process of purifying may be more complete, as there is no limit to the weight of the apparatus used for that purpose. The volumeter being filled with the pure gas is held at 0° and the exact pressure (about 760 mm.) is read. Then the gas is absorbed in a suitable apparatus, previously evacuated and weighed, and connected to the volumeter by a tight-fitting joint.

The densities of hydrogen (Morley), oxygen and sulphur dioxide (Jaquerod and Pintza) have been determined by the first method, by the second those of nitrous oxide, carbon dioxide and ammonia (Guye and Pintza), and, more recently, ammonia (Perman and Davies).

The volumeter method used does not take into account the correction for the contraction of the balloons, but only that necessary for the reduction of the weights to weights *in vacuo* (for the evolution or absorption apparatus is weighed with a counterpoise of the same glass and the same volume) and finally the pressure coefficient of the gas in order to calculate the volume at a pressure of 760 mm.

Whichever method is employed (balloon or volumeter), the correction for the pressure coefficient of the gas is negligible, since the pressure differs from 760 mm. by only a few millimeters.

found for the weight of a liter of these gases, determined simultaneously with two balloons.

WEIGHT OF A LITER OF NO (G. AND D.).

No. of observation.	Capacity of balloon. Liter.	Weight of 1 liter. Gram.
7	0.8	1.3401
7	0.4	1.3403
5	0.5	2.92666
4	0.3	2.92659

It may be claimed that this condensation was not on the surface of the glass, but in the special grease used to insure a tight cock. It may be well to cite here the recent work of Swinton (*Chem. News*, 95, 1349 (1907)), who has shown that the gases, hydrogen and helium, have no chemical action on the surface of glass, and that the surface condensation is of a purely mechanical nature. The recent observations of Travers (*Proc. Roy. Soc.* 78A, 9 (1906)) on the condensation of gases by solid bodies should not be overlooked, if the density of a gas is to be determined with an accuracy exceeding 1 part in 10,000.

Choice of a Unit.—A common unit is indispensable. Leduc has reduced his values either to the density with regard to air, or to the weight of a liter of gas at Paris, or both. Morley expresses his results in weight per liter under standard conditions, that is, at 0° and 760 mm. pressure, at sea level and latitude 45°. Rayleigh calculates his results either to density compared with air or compared with oxygen (taken equal to 32) or as the weight of 1 liter at London or at Paris. At Geneva the weight of the liter under standard conditions has been directly determined. Gray, as well as Perman and Davies, has likewise used this unit, which is the unit for all results which are given in the following pages.

D. Berthelot (*Compt. rend.*, **144**, 269 (1907)) has recently calculated the greater number of measurements, comparing densities to that of oxygen. Instead of taking one value for oxygen, he adopts, in each case, the value obtained by each investigator for the density of this gas. This system presents several disadvantages: First, in the case of those determinations made by investigators who have not determined the value for oxygen, the choice of such a value becomes somewhat arbitrary. Second, it might happen that the value for oxygen, even when determined by the investigator, was the most inaccurate of all his determinations; thus the accuracy of his other values would be diminished. This is the case, for example, at Geneva, where the value for oxygen has been determined with less precision than for the other gases.

These disadvantages disappear when all results are calculated to the weight of one liter of the gas under standard conditions. All the investigators, with the exception of Leduc, have recorded the exact volume of the balloons employed. Leduc's values may be calculated, since he has determined the weight of a liter of air at Paris.

There is, finally, another reason for expressing the density by the weight per normal liter, and that is the fact that the volume of the balloon can be calibrated more accurately than the weight, of a gas for comparison, can be determined in the same balloon. Leduc reports that after an interval of two years the capacity of a balloon originally found to be 2.27636 liters, was 2.27630 liters, or the variation was 1 : 38,000. At Geneva an accuracy of 1 part in 30,000 to 35,000, between successive calibrations, has been easily realized. It is necessary to determine the capacity of the balloon for water at 0°, and under these conditions no correction for the expansion of the glass is required.[1]

Choice of Final Values.—The following are some of the rules which have guided us in making a choice between the various values obtained for the density of each gas.

First, the nature of the method employed for the production and purification of the gas has been taken into consideration. This is, to our mind, the most important consideration in the density determinations. Those results showing concordance in the values obtained for the gas prepared in two or three different ways have, therefore, been given most weight.

[1] Difficulty was experienced in weighing the balloon filled with water at 0°, as the water expands when the balloon is placed on the balance. This has been overcome by attaching a bulb tube to the tubule of the balloon, by means of a ground joint or a rubber tubing, the whole apparatus having a counterpoise of the same glass and the same volume.

A second consideration, equally important, is the concordance obtained by different investigators for the same gas. When the average values of two observers agree, while that of a third experimenter differs by a considerable amount, they have not been given equal weight, but the third value has been given less weight than the first two. Frequently, an experimenter has made a more or less accurate determination of the limit of error of his work. We have applied the correction in such a way as to bring the value nearer the mean of the other two observers. Similarly, when an error was discovered in the course of subsequent work, we have not taken into account that value known to be erroneous.

As will appear in the following discussion, while the preceding rules are suggested, an accurate choice is difficult to make. We would add that in abandoning several of Leduc's values, giving preference to others, generally more recent, in their stead, there has been no intention of diminishing the importance of Leduc's work. If the modern determinations have benefited by a more perfect technique, still we must recognize that to Leduc belongs the credit of having been the first to give a complete solution, theoretical and experimental, of the problem of the rigorous determination of the molecular weights of gases as a function of their densities.

II. Discussion of Results.

Oxygen.—The system of atomic and molecular weights being referred to oxygen (O = 16), the exact determination of the density of this gas is of considerable importance.

Morley (*Z. physik. Chem.*, **20**, 1 (1896)) has made 41 determinations of this value, of which the averages of three series are:

Series.	No. of determinations.	Weight of a standard liter. Grams	Capacity of balloon.[1] Liters.
I.	9	1.42879	21.6 and 8.8
II. (*a*).....	6	1.42887	20.06 " 20.56
(*b*).....	9		
III. (*a*).....	7	1.42917	8.83, 16.52 " 15.38
(*b*).....	10		

In the first series the temperatures varied between 15° and 20°, measured with mercury and air thermometers, the apparatus being connected with a manometer open to the air. In the second, the balloons were submerged in pounded ice, and the pressure measured by a differential manometer. In the third, the balloons were submerged in ice, the pressure being read on a barometer, the cistern of which communicated with the interior of the balloon.

The oxygen was prepared from potassium chlorate and by electrolysis of a solution of caustic potash for Series III(*b*). The extreme variations between the individual observations were as follows:

$\frac{4.8}{10,000}$ for Series I, $\frac{2}{10,000}$ for Series II(*a*), $\frac{6.9}{10,000}$ for Series II(*b*), $\frac{6.8}{10,000}$ for Series III(*a*), $\frac{7}{10,000}$ for Series III(*b*). Referred to the averages, these extreme variations would be reduced to about one-half.

[1] Capacities are given in round numbers.

Morley gives double weight to the average of Series III, and thus arrives at the value, 1 liter oxygen = 1.42900 ± 0.000034.

Rayleigh (*Proc. Roy. Soc.*, **53**, 144 (1893)) used oxygen prepared by three different methods: (*a*) by heating a mixture of potassium chlorate and sodium chlorate; (*b*) by heating potassium permanganate; (*c*) by electrolysis of water, leading the gas thence through a column of copper oxide heated to redness. The balloon was filled at 0° under a pressure of about 1 atm. at London, its capacity being 1836.52 cc. The averages of the results (weight of oxygen contained in the calibrated balloon) for each series are:

Method.	No. of experiments.	Weight of oxygen. Grams.	Extreme error.
Chlorates (*a*)	5	2.6269	2.3/10,000
(*b*)	5	2.6269	2.3/10,000
Permanganate	3	2.6271	1.1/10,000
Electrolysis (*a*)	1	2.6271	.....
(*b*)	2	2.6272	.....
Average,		2.62704	
Correction for contraction,		0.00056	
Corrected weight,		2.62760	

1 liter of oxygen at Paris = 1.42952.

Dividing the value by 1.00033, the gravity factor, 1 normal liter of oxygen = 1.42905 grams.

Leduc (*Recherches sur les gaz*, Paris, 1898), using the balloon method, has reported the density relative to that of air, at Paris. He prepared the oxygen (*a*) by electrolysis of an aqueous solution of caustic potash or sulphuric acid, (*b*) by decomposition of potassium permanganate, (*c*) by electrolysis of dilute sulphuric acid, the gas then passing through a column of hot copper oxide.

By the method (*a*) the values, referred to air, varied between 1.10501 and 1.10516, average = 1.1051, extreme variation 1.4/10,000. By the method (*b*),[1] 1.10527; by the method (*c*) (3 determinations), 1.10521.

Rejecting the results for (*a*) Leduc adopts 1.10523 for the density of oxygen referred to air at Paris. From this the weight of the normal liter is $\frac{1.29316 \times 1.10523}{1.00033} = 1.42876$ grams (taking into account the weight of a liter of air at Paris, determined by the same investigator to be 1.29316, which he claims is accurate to 1/20,000); or in round numbers, allowing for the accuracy of 1/20,000 claimed by Leduc, 1 liter of oxygen = 1.4288 grams.

Jaquerod and Pintza (*Compt. rend.*, **139**, 129 (1904)), working in this laboratory, have made five determinations of the density of oxygen, obtained by heating potassium permanganate, by filling a volumeter of about 3.5 liters capacity, at 0° and about 1 atmosphere pressure. These determinations, showing an extreme difference of 6/10,000, give for the weight of the standard liter

1 liter oxygen = 1.4292.

[1] Leduc does not mention the number of determinations. It would appear that only one was made.

These determinations were made by the volumeter method. The authors consider their results to be a little too high, and for their further calculations have adopted the value 1.4290.[1]

Gray (*J. Chem. Soc.*, **87**, 1607 (1905)), in the course of his work on the density of nitric oxide, has made six determinations of the density of oxygen, which show remarkable agreement among themselves. The gas was prepared by heating recrystallized potassium permanganate. The results give for the weight of a balloon of 267.43 cc. capacity, filled at 0° and one atm. pressure at Bonn, the value 0.38228, the extreme variation being only 1.6/10,000. A correction brings the capacity of the balloon to 267.388 cc. so that the weight of a normal liter, taking into account the factor for the gravity at Bonn, is

$$1 \text{ liter of oxygen} = \frac{0.38228}{0.267388 \times 1.000505} = 1.42896 \text{ grams,}$$

a value differing from that of Morley's by only 1/36,000.

Résumé.—Morley's determinations, being the most numerous, and carried on under the most varied conditions, would appear to deserve the greatest weight, even though the individual variations are relatively large. Rayleigh's value is 1/20,000 greater than Morley's, while Gray's is 1/36,000 less. On the other hand, the less accurate work of Leduc and Jaquerod and Pintza differ from this by 1/7000, one greater and one less. Whether the mean of all five determinations, or of only the first three, which merit the greater confidence because of the greater number of single determinations and the close agreement between the single determinations, be taken, the value is the same—1.42900. The variations +0.00005 (Rayleigh) and —0.00004 (Gray), from the mean of Morley's values, are of the same order as the probable error calculated for the latter (+0.000034).

The value, 1 liter of oxygen = 1.42900, is therefore adopted, and is certainly correct to 1/10000 and probably to 1/20000.

Nitric Oxide.—Leduc (*Séances soc. franç. physique*, 1893, p. 214) determined the density of the gas in 1893, and reported it to be 1.0388 referred to air, from which the weight of a normal liter can be calculated to be 1.3429. Leduc suppressed this value in his memoirs published in 1898; therefore, it can hardly be taken into account. It is evidently too high. During the investigation carried on with M. Davila we obtained very nearly the same value when using a gas which had not been purified by liquefaction and fractional distillation, so that it would appear that such a high value is due to the presence of traces of nitrous oxide in the gas.

Gray was the first to make an accurate determination of the density of this gas, using the balloon method. The gas was prepared by the action of acetic acid on sodium nitrite and potassium ferrocyanide, washed with caustic potash, dried over phosphorus pentoxide, then liquefied and fractionated at low temperatures. Six determinations,

[1] D. Berthelot has recently reported all the density determinations made in this laboratory, referred to this unit 1.4292 (*Compt. rend.*, **144**, 260). In view of the few determinations made, and the reservations made by the authors, this has diminished the accuracy of our other results. In all our other work we have adopted the value 1.4290. See *J. chim. phys.*, **4**, 333.

showing an extreme difference of 3/10,000, gave as the weight of the gas contained in the balloon, 0.35851. Six determinations of oxygen (extreme variation 1.3/10,000) gave 0.38228. Adopting Rayleigh's value for oxygen (1.42905) the value for nitric oxide is calculated.

$$1 \text{ liter of nitric oxide} = \frac{1.42905 \times 0.35851}{0.38228} = 1.3402 \text{ grams.}$$

On the other hand, he calculates, from the capacity of the balloon,[1] 1 liter of nitric oxide = 1.34011 and 1 liter of oxygen = 1.42896. Gray adopts the value 1.3402 grams. This practically conforms with that which would result if the value O_2 = 1.42900 were used.

$$1 \text{ liter NO} = \frac{1.4290 \times 0.35851}{0.38228} = 1.34015.$$

Guye and Davila have carried out three series of determinations on gas prepared from three different sources, (*a*) by the action of ferrous sulphate on nitric acid; (*b*) by decomposition by means of mercury of a solution of sodium nitrite acidified with sulphuric acid; (*c*) by the action of sulphuric acid on a concentrated solution of sodium nitrite. The method of purification was in each case the same as that employed by Gray, with the exception that the washing with caustic potash was omitted, as it changes a part of the gas to nitrous oxide.

Weighings were made in two balloons of about 0.8 and 0.4 liter capacity, respectively.

Method.	No. of experiments.	Weight of 1 liter.	Extreme error. Large balloon.	Extreme error. Small balloon.
Mercury	6	1.3403	3/10,000	6.7/10,000
Ferrous sulphate	6	1.3402	3/10,000	4.5/10,000
Sodium nitrite	2	1.3401	3/10,000	

The mean of the 14 experiments, together with the mean for each method, gives 1 liter NO = 1.3402, a value identical with Gray's and which we hereby adopt.

Carbon Dioxide.—Rayleigh reports the density of this gas to be 1.52909 as referred to air. He gives no details as to the method, the number of determinations, or their probable error. The gas was prepared, (*a*) by the action of hydrochloric acid on marble, (*b*) by the same acid on sodium carbonate.

Leduc obtained the mean value of 1.52874 for three very concordant determinations on a gas prepared by the action of hydrochloric acid on marble. He adopts the value 1.5288, in view of the probable error due to traces of air. He also observes that the work of Regnault points to the value 1.5290.

The value for a normal liter can then be deduced as follows:

$$1 \text{ liter of } CO_2 = 1.29284 \times 1.52909 = 1.9769 \text{ (Rayleigh).}$$

$$1 \text{ liter of } CO_2 = 1.29273 \times 1.5288 = 1.9763 \text{ (Leduc).}$$

Guye and Pintza have determined the weight of a normal liter directly, with a gas generated by heating sodium bicarbonate, and have found 1.9768, the mean of three experiments having an extreme difference of 0.8/10,000. The value finally accepted,

$$1 \text{ liter of } CO_2 = 1.9768,$$

[1] By private communication.

agrees to about 1/20,000 with Rayleigh's value; it gives a certain weight to the lower result of Leduc and is justified by a consideration of the probable error. In the course of the work at Geneva, the difficulty experienced in obtaining carbon dioxide entirely free from air has been constantly kept in mind, and the gas which was used in these determinations was entirely soluble in cautic potash.

Nitrous Oxide.—Leduc, Rayleigh, and Guye and Pintza have determined the density of nitrous oxide.

Leduc used the commercial[1] liquefied gas, rectified by distillation. He obtained the densities, referred to air, of 1.5304, 1.5298, 1.5301. Average, 1.5301; extreme error, 3.9/10,000. Rayleigh made his first series of determinations in 1897 with a gas obtained by the decomposition of ammonium nitrate, and purified by dissolving in water—heating to expel the gas, then drying. Five determinations, with a probable error of 1.7/10,000, gave the mean value 1.52951 referred to air. In 1904 Rayleigh (Rayleigh, *Proc. Roy. Soc.*, **74A**, 181) repeated his work, using the commercial liquefied gas, purified in the same way as above, and obtained practically the same result. He then purified the commercial gas by fractional distillation at the temperature of liquid air, till the density remained constant, and obtained, as the mean of three very concordant observations, with an extreme difference of 0.8/10,000, the value 1.5297.

From this last value of Rayleigh's and from Leduc's, the following values for the weight of the normal liter may be calculated:

$$1 \text{ liter of } N_2O = 1.9780 \text{ (Leduc)},$$
$$1 \text{ liter of } N_2O = 1.9777 \text{ (Rayleigh)}.$$

Guye and Pintza have determined the weight of the normal liter directly, using the volumeter method. The gas was prepared by the double decomposition of hydroxylamine sulphate and sodium nitrite. The average of three experiments, having an extreme variation of 2.8/10,000, is

$$1 \text{ liter of } N_2O = 1.9774 \text{ (Guye and Pintza)}.$$

The impurities which might be found in the commercial nitrous oxide are nitrogen peroxide, air or nitrogen. The fractionation at low temperatures might not bring about a complete elimination of these impurities,[2] or it might be that the decomposition of hydroxylamine sulphate did not furnish a gas entirely free from air, even though the evacuation of the apparatus was repeated several times. Under these conditions, and considering the good agreement of the separate determinations made by Rayleigh in 1904, we would adopt for the weight of the normal liter,

$$1 \text{ liter } N_2O = 1.9777 \text{ grams},$$

which is the mean of the values obtained by Rayleigh, Leduc, Guye and Pintza.

Hydrochloric Acid Gas.—Leduc has determined the density of hydrochloric acid gas, produced by the action of sulphuric acid on sodium chloride, and dried over phosphorus pentoxide, to be 1.2692 as compared with air. There is no indication of the number of determinations or

[1] Obtained by heating ammonium nitrate.

[2] The washing with alkalies, as practiced commercially, is not sufficient to remove the last traces of NO_2.

their accuracy, although he considers the last decimal doubtful. A normal liter would be 1.29273 × 1.2692 = 1.6407 grams.

Guye and Gazarian have repeated this determination with a gas prepared in the same way, but further purified by liquefaction at the temperature of liquid air and fractionation at a low temperature.[1] A preliminary series of four determinations gave a mean of 1.6398, with an extreme variation of 9/10,000.

Gray, who has undertaken a revision of the density of hydrochloric acid gas, reports a series of six determinations, with a probable error of 3.7/10,000, of which the mean is, one normal liter = 1.6397. This differs from the preceding by 1/16,000. The mean of these two concordant values would be 1.63975 or, suppressing the last decimal, 1.6398. This value is given only provisionally, until further determinations shall be announced.

Ammonia Gas.—Leduc used ammonia gas obtained from a commercial ammoniacal solution called "pure," which he dried over molten caustic potash. Without reporting the number or the accuracy of his determinations, he gives the value 0.5971 as compared with air, or the weight of one normal liter,

$$1.29273 \times 0.5971 = 0.7719 \text{ gram.}$$

Guye and Pintza have determined the weight of a standard liter, using commercial liquefied ammonia. Assuming that Leduc's high value was due to the presence of organic bases, these experimenters previously purified the gas by leading it over red-hot quicklime, to transform the nitrogen of the organic bases into ammonia. The gas was then collected as ammonium chloride, in this form was recrystallized, and was finally set free by warming the salt with lime, and dried over long columns of recently molten caustic potash. It was entirely soluble in sulphuric acid. Five determinations (using a volumeter of 3.5 liters capacity) with an extreme error of 3.9/10,000 gave a mean value 0.77079, or in round numbers, 1 normal liter = 0.7708. Perman and Davies (*Proc. Roy. Soc.*, **78A**, 34 (1906)) have repeated this determination, both by the volumeter method, using a balloon of 1.7783 liters capacity, and by the balloon method, using a balloon of 0.50476 liter capacity. With the gas from a commercial ammoniacal solution, repeating Leduc's procedure, they have arrived at a value 0.7717, almost identical with Leduc's, thus proving the necessity for removing the organic bases. They then purified the gas by three different methods; (*a*) by the method of Guye and Pintza, (*b*) by decomposing with caustic potash, ammonium oxalate which had been ten times recrystallized, (*c*) by reduction of sodium nitrite, in a caustic soda solution, by aluminum. They obtained the following results:

Method.	No. of experiments.	Weight of 1 liter.	Extreme error.
Volumeter, prepared by (*a*), (*b*), (*c*)	7	0.77085	5.2/10,000
Balloon, prepared by (*a*)	4	0.77086	0.8/10,000

[1] These fractionations were for the purpose of eliminating the volatile phosphorus compound, which, according to Richards and Wells (This Journal, 27, 459) is formed when hydrochloric acid passes over phosphorus pentoxide, and which would increase the density of the gas. Our work has also shown that the desiccation of the inside walls of the balloon is accomplished only after repeated rinsings with the hydrochloric acid gas. For these reasons Leduc's value must certainly be a little too high.

The extreme error in the first series is undoubtedly due to the fact of the ammonia gas having been prepared by several methods. The authors advise the value 0.77085.

It appears from these experiments that Leduc's value cannot be considered in deciding upon a final value, as it is unquestionably affected by a constant error due to the presence of organic bases. The mean of the other three values is 1 liter of ammonia = 0.770837, which can be taken in round numbers to be

$$1 \text{ liter of ammonia} = 0.7708,$$

differing from the above by 1/19,000. It takes into account the fact that any source of error (presence of air or of organic bases, traces of moisture or condensation on the surface of the balloon)[1] would tend toward raising the final value rather than lowering it. The mean of the determinations by Perman and Davies, using the volumeter method, which they consider most accurate, and gas prepared by method (*a*), is 0.77080 gram.

Sulphur Dioxide.—Leduc reports 2.2639, referred to air, as the mean of several determinations (he does not state the number) having an extreme variation of 1.3/10,000. The gas was prepared by the action of mercury on pure sulphuric acid.

Jaquerod and Pintza, using the volumeter method (capacity of balloon = 3.5 liters) and a gas prepared by repeated fractional distillations of the liquefied sulphur dioxide of commerce, have obtained as the weight of one normal liter of sulphur dioxide 2.9266 grams, which represents the mean of seven determinations having an extreme difference of 1.7/10,000.

This result agrees exactly with Leduc's,

$$1 \text{ liter of sulphur dioxide} = 1.29273 \times 2.2639 = 2.9266.$$

Baume, using two balloons of 0.3 and 0.5 liter capacity, respectively, has recently repeated this determination in the Geneva laboratory and obtained the same result. The gas was purified by the same method as that employed by Jaquerod and Pintza. The extreme variation was 3.8/10,000 for the large and 12.7/10,000 for the small balloon. The mean of the two series is

$$1 \text{ normal liter} = 2.9266.$$

This, therefore, is the accepted value.

Conclusions.

The various results have been tabulated as follows: In column I are the values obtained by Leduc; in column II those obtained by Rayleigh; in column III those of various other investigators (Morley, Ramsay, Gray, Perman and Davies); in column IV those obtained in the Geneva laboratory; in column V the finally accepted value; in column VI the same value referred to the density of oxygen as one. This table has been com-

[1] Of the three methods, (*a*), (*b*), (*c*), the first would undoubtedly give the purest gas. The recrystallization of ammonium oxalate does not assure a complete elimination of organic bases, which is likewise true of the reduction of sodium nitrite by aluminum, as the latter may contain small amounts of carbon capable of being transformed into organic bases. In the course of my work with Pintza we proved conclusively that the ammonia gas obtained by the decomposition of magnesium nitride contained traces of organic bases. Its density was 1/1935 higher than that of the gas prepared by method *a*.

pleted by the addition of the better recent determinations of other gases (*J. chim. phys.*, 5, 203 (1907)):

WEIGHT OF NORMAL LITER (IN GRAMS).

Gas.	Leduc	Rayleigh.	Others.	Laboratory. Guye.	Accepted value.	Referred to density of O_2.
O_2	(1.4288)	1.42905	1.42900 M. 1.42896 Gr	(1.4292)J.P.	1.42900	1.00000
H_2	0.08982	(0.08998)	0.089873 M	.....	0.08987	0.062890
N_2	1.2503	1.2507	1.2507 Gr	.....	1.2507	0.87523
CO	1.2501	1.2504	.....	.....	1.2504	0.87502
NO	(1.3429)	.....	1.3402 Gr	1.3402 G.D.	1.3402	0.93786
Ar	.....	1.7809	1.7808 R	.....	.....	1.2463
CO_2	1.9763	1.9769	.....	1.9768 G.P.	1.9768	1.3833
N_2O	1.9780	1.9777	.....	1.9774 G.P.	1.9777	1.3840
HCl	(1.6407)	.....	1.6397 Gr	1.6398 G.G.	1.6398	1.1475
NH_3	(0.7719)	.....	0.77085 P.D.	0.7708 G.P.	0.7708	0.53940
SO_2	2.9266	.....	.....	2.9266 J.P. 2.9266 B.	2.9266	2.0480
Air	1.2927	1.2928	.....	.....	1.2928	0.90469

[1] Dapier, *J. chim. phys.*, 5, 203 and *Arch. sci. phys. nat.* [4], 24, 34.

The conclusions to be drawn from the work carried on at Geneva during the last three years, compared with that accomplished in other laboratories, are as follows:

1. The method gives results generally agreeing to at least 1/10,000, when one takes the mean of a half dozen determinations, the extreme difference between any two of which is not more than 3/10,000 or 5/10,000.

2. This agreement may be obtained even with gases as difficultly dried and purified as ammonia, hydrochloric acid, sulphur dioxide or nitric oxide. For these it is only necessary that the balloon be well dried with dry air, and then rinsed several times in succession with the dry gas which is to be studied. Under these conditions there is no appreciable difference between the mean obtained for a balloon of 3.5 liters capacity and one of 0.5 liter. The surface action is then negligible in work of an accuracy of the order of 1/10,000.

3. The purification of the gas is especially important. The method based on the liquefaction of the gas, followed by distillation at low temperature, is recommended.

4. It is preferable to calculate directly the weight of a liter of the gas under standard conditions, rather than to report the density as compared with that of another gas (oxygen or air). By calibrating the balloon at 0°, its volume may be determined to 1/30,000—an accuracy which could be approached, in the density determination, only by a very considerable number of determinations.

5. The most probable values for the density of the gases, determined with an accuracy of the order of 1/10,000, are collected in columns V and VI of the last table.

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NEW BOOKS.

ANNUAL REPORTS ON THE PROGRESS OF CHEMISTRY FOR 1906. Issued by the Chemical Society. Vol. III. London: Gurney and Jackson. 1907. 387 pp. Price, $2 net.

The arrangement of the material in this, the third, volume of these epitomes of the progress of a year along each of a number of lines of chemical science is the same as that previously employed, and the reports are written by the same authors as in 1905, with the exception of that upon General and Physical Chemistry, which is prepared by A. Findlay instead of James Walker.

General and Physical Chemistry are treated apart from Inorganic Chemistry; Organic Chemistry is subdivided into aliphatic, homocyclic, and heterocyclic divisions, and Stereochemistry is separately treated. Analytical, Physiological, and Mineralogical Chemistry, and Radioactivity, each has a separate reviewer, while Agricultural Chemistry and Vegetable Physiology are combined in one report.

As in the earlier volumes of this series, an effort has been made to render the reviews readable and more attractive than a mere compilation of data. The results are excellent, and seem to have been attained without sacrifice of accuracy. It is almost inevitable that such a presentation should involve the frequent expression of the personal convictions of the authors, and it is not surprising that these should, at times, become a bit obtrusive. As between this evil and a prosy cataloguing of articles, the reader will quickly accept the style adopted in this volume as the less objectionable, particularly since the authors may claim to speak with authority in their respective fields.

These reports include only notices of papers which represent an advance in our knowledge of chemical science. The selections made by the respective authors appear to be wisely chosen, and the statements, necessarily very concise, are adequate to lead the reader to institute further search among the original papers, when his interest is aroused. The volume as a whole constitutes a valuable aid to the busy worker. It would seem to the reviewer that, in spite of the references to industrial chemical progress which are included in the Reports as now subdivided, they would gain in value to the technical chemist, if a review devoted to Industrial Chemistry were added. This field is, of course, exceedingly broad, but with the same judicious selection of topics which is shown in the present reviews, the important advances of the year might well be brought within proper compass. The fact that this field is covered in another journal in English does not seem to entirely excuse its omission from these volumes. H. P. TALBOT.

ORGANIC CHEMISTRY, INCLUDING CERTAIN PORTIONS OF PHYSICAL CHEMISTRY, FOR MEDICAL, PHARMACEUTICAL AND BIOLOGICAL STUDENTS (WITH PRACTICAL EX-

ERCISES). By H. D. HASKINS, A.B., M.D., Instructor in Organic and Bio-Chemistry, Medical Department, Western Reserve University; Professor of Chemistry, Cleveland School of Pharmacy, and J. J. R. MACLEOD, M.D. (Aberdeen), D. P. H. (Cambridge), Professor of Physiology, Western Reserve University. New York: John Wiley and Sons. London: Chapman and Hall, Limited, 1907. Small 8vo. xii + 367 pp. Price, $2.00.

This text-book aims to give not only the facts of organic chemistry (with instructions for laboratory exercises) but also the most important facts of physical chemistry which have an essential bearing on medical science. The introductory chapters on physical chemistry are well written and on the whole correct (see, however, an error in the last paragraph on p. 43 in regard to the osmotic pressure of a solution), and they aroused the expectation of finding an equally well written short text on organic chemistry. As in many recent similar texts, there is much that is thoughtful and praiseworthy in the discussion of structures and the development of the experimental evidence in favor of given structures and in the ordinary treatment of organic chemistry; but one is disappointed in finding in a book that aims to include in its work a few of the fundamental concepts of physical chemistry so little of its spirit *realized* in the treatment of organic reactions; for instance, the old superficial parallel in the equations of ester and salt formation is emphasized (p. 93) and the esters are still called "ethereal salts" "comparable with the salts of inorganic chemistry," (p. 125), although they have none of the properties of salts. It is true that the differences in behavior and formation of esters and salts are *mentioned*, but the authors do not seem to have had the courage to break with the old, wrong conception and thus there is left a confusing impression on the reader. Aside from a brief discussion of the reversibility of esterification and saponification, no use whatever is made of the facts of reversibility and equilibrium in this book, although they are of especial importance for physiologists and are essential in a book that claims to use the modern concepts of physical chemistry. In part, even the ordinary treatment of purely organic topics is decidedly faulty; the emphasis laid on the proportion of hydrogen and oxygen in the carbohydrates (p. 209) is misleading and gives a wrong conception of the essential nature of carbohydrates. In no place, for instance, is any mention found of the true sugar group —CH(OH)—CO— and from misleading remarks about the reducing power of ketones (pp. 138 and 216) it appears the authors are not clear in their own minds about the reducing power of the "sugar group." On page 214 we are told that there are *eleven* stereoisomeric acids having the structure $HOOC.(CHOH)_4COOH$! The most glaring fault of the book is in the language used in giving the instructions for laboratory work (see pp. 85, 86, etc.); they are not written in English but in the laboratory jargon which is the pitfall for most fresh

young doctors of philosophy in writing their dissertations and which makes abominable reading! So while the book was undertaken in a praiseworthy attempt to bring the subject of organic chemistry into closer relationship to the modern conceptions of physical chemistry, it is hardly a success in this respect and is only of average value and in part badly written as an ordinary text-book of organic chemistry.

JULIUS STIEGLITZ.

UNIVERSITY OF CHICAGO,
November 16, 1907.

A TEXT-BOOK OF ORGANIC CHEMISTRY. By A. F. HOLLEMAN, PH.D., F. R. A., Amsterdam, Professor Ordinarius in the University of Amsterdam. Translated from the Third Dutch Edition by A. J. WALKER, PH.D., assisted by OWEN E. MOTT, PH.D., with the coöperation of the author. Second English Edition, Rewritten. New York: John Wiley & Sons. London: Chapman and Hall, Limited. 1907. 8vo. xv + 589 pp. Price, $2.50.

According to the author's preface to this second English edition of his text-book on organic chemistry, the chief changes made are in the chapters on the constitution of benzene and on pyrrole. In presenting the vexed question of the constitution of benzene the plan is adopted of giving all three of the most prominent formulae, Kekulé's, von Baeyer's and Thiele's, with an explanation and a very brief criticism of each.

There is legitimate ground for a wide divergence of opinion in regard to the best order of arrangement for the presentation of the facts of organic chemistry. It seems to the writer, however, that with the facts of isomerism and the theories of structure, stereoisomerism and tautomerism,[1] the fundamental point which must be most clearly understood by the student for a working acquaintance with organic chemistry is the difference in behavior between saturated and unsaturated compounds. This difference is brought out most effectively from the experimental and theoretical side, by a study of the properties of the unsaturated hydrocarbons. The point of view acquired there is most useful, in fact, essential, in the study of the reactions of the aldehydes and ketones as unsaturated compounds, in which absorption reactions play an extremely important rôle, in which the smaller degree of stability of the addition products involves no difficulty in presentation after a thorough discussion of the olefines and acetylenes, and in connection with which relative instability, a further fundamentally important point of view for organic as for inorganic chemistry may so easily be developed; namely, the conception of organic reactions as reversible ones, which should be treated

[1] This question is treated on p. 305, and the discussion is restricted to the 1:3 diketones. It is a question affecting very many important classes of organic compounds (acid amides, nitroparaffins, mono-aldehydes and ketones and their hydrazones and oximes, phenols, etc.), and it seems to the writer that *in a book of this class*, it ought to be taken up as a part of the question of isomerism at as early a point as possible.

on the basis of the equilibrium laws. A modern comprehension of the behavior of organic acids and their derivatives, the esters, amides, nitriles, etc., it seems to the writer again, is altogether impossible without a preliminary knowledge of the behavior of aldehydes, ketones and olefines, unsaturated bodies whose absorption products are so far more stable than the absorption products of the derivatives of the organic acids, which nevertheless must play an important rôle in the proper theoretical treatment of their reactions. Yet we find in Holleman's text the order of treatment exactly reversed, the acids with their most complex behavior first, the olefines with their well-defined simple properties treated only after such complex unsaturated bodies as the nitriles, isonitriles, acids and their derivatives, aldehydes and ketones. There is room, it is believed, for a text-book on organic chemistry in which the reactions are treated on the basis of our equilibrium laws in a very simple and elementary but efficient way with the aid, not of hypotheses, but of well-known simple facts.

JULIUS STIEGLITZ.

THE UNIVERSITY OF CHICAGO,
Nov. 16, 1907.

POISONS, THEIR EFFECTS AND DETECTION. By A. WYNTER BLYTH AND M. W. BLYTH. London: Charles Griffin & Co., 4th Ed. 1906. 8vo. xxxii + 772 pp. Van Nostrand Company. Price, $7.50 net.

The announcement by the publishers of a forthcoming new edition of this standard work aroused great interest among analysts and toxicologists, and they awaited the appearance of the work with the curiosity natural to the interval of ten years between editions. The fact that Blyth's poisons is the only comprehensive work of its kind in the English language should make a new edition doubly valuable.

The fourth edition carries an additional name upon its title-page—that of Meredith Wynter Blyth, Public Analyst for the Boroughs of Brighton and Eastbourne. This would lead one to conclude that the presence of poisonous substances in food products and the relations of such materials to the public health would receive more attention than was accorded them in the third edition. In this, however, we suffer a very great disappointment, for this phase of the field of the toxicologist and investigator is practically ignored, there being essentially no change in the subject-matter treated, the additions and alterations being mainly in the arrangement and elaboration of contents of the old edition. However, these changes in the manner of presentation and the addition of newer and better methods of chemical analysis are sufficiently numerous and extensive to justify the claim of the publishers that the fourth edition is "thoroughly revised, enlarged, and rewritten."

The work is divided into nine "parts" as follows: I. Introductory, the old Poison-Lore, the Growth and Development of the Modern Methods

of Chemically Detecting Poisons; Bibliography. II. Definition of Poison; Classification of Poisons, Statistics, Connection between Toxic Action and Chemical Composition; Life Tests; General Methods in Searching for Poison; the Spectroscope as an Aid; Examination of Blood Stains. III. Poisonous Gases. IV. Acids and Alkalies. V. Substances Capable of being Separated by Distillation. VI. Alkaloids and Poisonous Vegetable Principles. VII. Poisons derived from Living or Dead Animal Substances. VIII. Oxalic Acid Group. IX. Inorganic poisons.

Appendix—Treatment of Cases of Poisoning. Domestic Ready Remedies for Poisons.

Parts I and II are thus devoted to the discussion of what may be called General Toxicology, the remaining parts to Special Toxicology.

Part I has been much improved, both by the addition of new material and the suppression of doubtful facts; thus revised, the chapters are more readable. Following Part I is to be found a bibliography of the chief works on toxicology, which unfortunately has neither been revised nor brought down to date, only a single addition—Vibert's Précis de Toxicologie—has been made to the works listed ten years ago.

Part II has had much new matter added to it. The arrangement of the classification of poisons has been changed by a more logical combination of doubtful substances under a single group—Vegetable Principles Not Readily Admitting of Classification—and in this group have been placed Tutin, Illicium Religiosum, Picric Acid and Picrates, Ictrogen, Lathyrus Sativus and Arum Poison, toxic substances not treated in the third edition. A further addition is found under poisons derived from animal substances in a sub-group—Mammalian Poison; Epinephrine. The statistics—Deaths from Poisons in England and Wales—are now for the period 1893–1903, the older statistics being suppressed.

The discussion of the relation between chemical composition, chemical properties and toxic effect has been extended and is an excellent summary of the facts now known, save for the omission of all mention of the contributions of physical chemistry to our knowledge of how toxic substances act upon living cells. There are also many other portions of the work where the introduction of physico-chemical methods and theories is greatly to be desired.

The chapter on Blood and Blood Stains has been entirely rewritten and Formanek's excellent charts of the absorption spectra of blood pigments have been reproduced, so that the analyst is now given reliable data and guidance to enable him to undertake an examination of suspected material with a fair prospect of success.

As might be expected, the authors have made the greatest changes in the specialized portions of their book. Improved methods of separation, identification and determination are to be met with in the case of almost

every poisonous substance discussed. The chapters devoted to the vegetable alkaloids are completely rewritten and greatly elaborated by the introduction of the latest knowledge relating to the chemistry of these substances. An exceedingly valuable feature is the introduction of structural formulas and an indication of the relationships of allied compounds. In the third edition the chapters devoted to the compounds of carbon were, on the whole, the most unsatisfactory portions of the book, but the authors have succeeded in the fourth edition in well rounding out their work. The analytical methods are now well chosen, both on account of their convenience and reliability.

Considering the number of very rare and utterly unimportant poisons of organic origin treated it is to be regretted that many common poisons have been omitted; most prominent among these may be mentioned formaldehyde, methyl alcohol, and acetanilide and other dangerous heart depressants.

The general make-up and typography of the work is excellent, there being remarkably few typographical errors; the only serious one noted by the reviewer is the formula—$NiCO_4$—ascribed to nickel carbonyl.

Providing the analyst does not regard the work as authoritative on chemical properties and industrial processes, he will find it a safe guide for the detection of toxic substances and a source of valuable information relative to physiological effects. Blyth's poisons should be in the library of every analytical chemist. E. M. CHAMOT.

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OF THE

American Chemical Society

AMERICAN CHEMICAL SOCIETIES.[1]

BY MARSTON TAYLOR BOGERT.

There are many ways in which a man may endeavor to serve his age and generation by devotion to the science of chemistry, and surely, not the least important of these is the labor which has for its object the stimulation and development of our great national chemical society, an organization which has been one of the most potent factors in the growth and progress of the science.

Among the prime requisites for the success of any organization are: (1) community of interest, and (2) an enthusiastic and intelligent coöperation on the part of the membership. That we all have the same interests at heart—the advancement of chemistry, and the development of our Society for this purpose—is true beyond any shadow of doubt. The needed coöperation on the part of the membership has been manifest in a high degree. Those who were fortunate enough to be present at our recent meeting in Toronto will, I know, bear testimony to the fine enthusiasm and *esprit de corps* evident. That is the spirit that should permeate the entire organization and penetrate to all corners of our country wherever our members are located, for it is certain to bring a rich harvest of growth and power to the Society.

In the rapid progress of our Society during the past few years, it has not been an easy matter to keep the members properly informed as to its exact condition and the lines of contemplated development, and yet without such information intelligent coöperation is difficult.

For any adequate comprehension of the requirements of an organization of the size and character of the American Chemical Society, not only is a searching scrutiny of its own history for the last thirty-three years neces-

[1] Presidential address delivered at the Chicago Meeting of the American Chemical Society, January 1, 1908.

sary, but also a careful consideration of past and present conditions of chemical organization in this country. On such knowledge as the foundation, it should be possible to base a fairly trustworthy judgment as to the most promising lines of development.

I have, therefore, made as thorough an examination as my time would permit of the history of chemical organizations in this country, partly that we might benefit by the experience of others, and partly to gather facts concerning other existing chemical organizations in the United States, in the earnest hope that a way may later open for the union of all American chemical organizations in one great society or federation.

It seemed to me that the subject was one of sufficient interest and importance to constitute an acceptable presidential address, for the next few years will be critical ones for us, and the more familiar our members are with such matters the more intelligently will they be able to assist our Council. Such a topic enjoys the obvious merit of appealing to every member present, an advantage which, I fear, would scarcely pertain to a text selected from my own chosen field of synthetic organic chemistry.

In the early history of our country, when it was striving to win for itself a place among the nations, there was little opportunity for the pursuit of science for science's sake. The facilities for acquiring chemical knowledge were necessarily very meagre, what little training there was, being given mainly in medical schools. Chairs of Natural History and Physical Science were generally held by physicians, for it was felt that their education more nearly fitted them for such work. Thus chemistry in the early days was largely a side issue, being taught often with *materia medica*. It is particularly interesting to me as a Columbia man to find that chemistry was first recognized as a branch of the curriculum of medical study at King's College (now Columbia) in 1767. In 1774, the Right Rev. James Madison was Professor of Chemistry and Natural Philosophy at Williams and Mary. The first separate Chair of Chemistry at a non-medical institution was established October 1, 1795, at the College of New Jersey (now Princeton). It was filled by Dr. John MacLean, from whom the elder Silliman received his early chemical instruction.

Although the latter half of the 18th Century was the period of Franklin, Rumford and Priestley, when we recall that this was also the period of our war for independence, it is not surprising that progress in science was relatively inconsiderable.

It was natural in these early years of science in America that what scientific organizations there were should be general in their character, as scarcely any individual science, with the possible exception of medicine, was strong enough to stand alone. It is appropriate, therefore, that a

few words be said about these general scientific societies before passing on to those strictly chemical.

The first of these general societies was the American Philosophical Society, founded by Benjamin Franklin, at Philadelphia, in the year 1743, and recognized by Provincial Charter in 1769. Franklin was its president from the date of its charter until his death in 1790. The first volume of its *Transactions* appeared in 1769 and contained a paper by Dr. DeNormandie on "An Analysis of the Chalybeate Waters of Bristol in Pennsylvania," which appears to be the first chemical analysis ever published in this country; and what are probably the first papers published by Priestley on this side of the water, entitled "Experiments and Observations Relating to Analysis of Atmospheric Air" and "Generation of Air from Water." This venerable association is still active and vigorous, its aim being to cover all branches of so-called natural science.

On May 4, 1780, the American Academy of Arts and Sciences was incorporated at Boston.

In 1799, the Connecticut Academy of Arts and Sciences was established at New Haven and incorporated by legislative enactment.

The Literary and Philosophical Society of New York, founded in the early part of the 19th Century, had but a brief existence, and published but a single volume of *Memoirs* (containing one paper on chemistry).

On April 20, 1816, the New York Lyceum of Natural History was incorporated. In 1876, it changed its name to the New York Academy of Sciences.

At about the same time, the Philadelphia Academy of Natural Sciences was established, the first volume of its journal appearing in 1817.

These early organizations were rapidly augmented by the establishment of various scientific associations and academies in other parts of the country, and most of our great cities now have one or more of this class.

The first of these general scientific organizations to wield more than a merely local influence and power was the American Association for the Advancement of Science. The original progenitor of this association was the American Association of Geologists, founded in 1840 by those engaged in the geological surveys of various states. It later became the Association of American Geologists and Naturalists, which body, at its meeting in Boston, 1847, resolved to enlarge its sphere of action to include physics, chemistry, astronomy, and the allied physical sciences, and thus began its enlarged existence in 1848 as the American Association for the Advancement of Science.

In most of these general organizations, it was customary to subdivide science more or less closely into sections. At the outset, chemistry was grouped frequently merely under the general section of natural sciences, then with physics or *materia medica*, and finally it was found necessary

to establish separate sections for chemistry. In the American Association for the Advancement of Science a chemical sub-section was established at the Hartford meeting, August 17, 1874, with S. W. Johnson as Chairman, and F. W. Clarke as Secretary. This became a full-fledged section (Section C) at the Montreal meeting of the Association, 1882, with H. C. Bolton as presiding officer and Alfred Springer as secretary.

CHEMICAL SOCIETY OF PHILADELPHIA.

The first organization devoted specifically to chemistry was the Chemical Society of Philadelphia, founded in 1792. This was probably the earliest chemical organization in the world, as it was born forty-nine years before the first European chemical society (Chemical Society of London, 1841). Priestley appears to have been one of its active members. In 1801–'02 its president was James Woodhouse, who was at the time Professor of Chemistry in the Medical Department of his *alma mater*, the University of Pennsylvania. This Chair had been held by Dr. James Hutchinson, and on his death, in 1793, was offered to Dr. Joseph Priestley, who had but just arrived from England. Priestley, however, preferred the quiet and retirement of Northumberland, and Dr. Woodhouse was then elected to the position. The most important communication presented to this society was that announcing the discovery of the oxyhydrogen blowpipe. It was made on December 10, 1801, by Robert Hare, Jr., then but twenty years old, who subsequently became Professor of Chemistry in the Medical School of the University of Pennsylvania. Just when this society ceased to exist is uncertain, but it appears to have been about 1803.

COLUMBIAN CHEMICAL SOCIETY.

It was succeeded by the Columbian Chemical Society of Philadelphia, founded August, 1811, by "a number of persons desirous of cultivating chemical science and promoting the state of philosophical inquiry." Its first president was James Cutbush and its membership list included sixty-nine honorary and thirteen junior members. Vol. I of its *Memoirs* appeared in 1813. As "patron" of this society appears the name of Hon. Thomas Jefferson, Esq., who had been president of the American Philosophical Society for many years, relinquishing it finally to become the President of the nation. Seventeen months before the founding of this society, he had retired from the presidency of the United States and was living at his country seat in Monticello. James Cutbush was at the time Professor of Natural Philosophy, Chemistry and Mineralogy at St. John's College. From June 1820 until his death, December 15, 1823, he taught at the U. S. Military Academy, West Point.

The constitution of this society provided in addition to other officers an "orator," who should deliver "an oration on some chemical subject

within two months after the commencement of the medical lectures in the University of Pennsylvania, in each year." As the *Memoirs* of the society contain no "oration," it has been suggested that the incumbent's efforts were not satisfactory. The roll was called at the opening and closing of every meeting and all absentees were fined twelve and a half cents each. Any member elected to office and declining to serve was fined one dollar. Once in each month the society appointed some member to read an original chemical essay, "for neglect of which, the member so appointed shall be fined one dollar." Candidates for admission were required to "read an original essay on some chemical subject."

Among its members were, Dr. Benjamin Smith Barton, of the University of Pennsylvania, sometimes called "the father of American natural history;" Dr. Archibald Bruce, of Columbia College, founder of the *American Mineralogical Journal*; Dr. John Griscom, "the acknowledged head of all teachers of chemistry in New York City" for more than thirty years; Robert Hare, of the University of Pennsylvania; Dr. David Hosack, of Columbia College, founder of the first public botanical garden in the United States (1801); James Madison, President of the United States; Dr. John Maclean, first Professor of Chemistry at the College of New Jersey; Hon. Samuel L. Mitchell, Professor of Chemistry and Natural History at Columbia College and a United States Senator; Dr. Benjamin Rush, of the University of Pennsylvania, who was regarded by Benjamin Silliman as "undoubtedly the first Professor of Chemistry in America," his appointment dating August 1, 1769; Benjamin Silliman, Professor of Chemistry at Yale; and many noted foreign chemists. This was the first chemical society of a truly national character. Unfortunately, it survived but a few years.

DELAWARE CHEMICAL AND GEOLOGICAL SOCIETY.

The Delaware Chemical and Geological Society was organized at Delhi, Delaware County, N. Y., September 6, 1821. It is stated that it was composed of "between forty and fifty well-informed and respectable inhabitants" of Delaware County. Its first quarterly meeting was held at Edgerton's Hotel in Delhi Village, with Charles A. Foote as president. It, too, was short-lived.

So far as the writer is aware, there were no important chemical societies in existence, certainly none of national influence, between this time and the founding of the Manufacturing Chemists' Association of the United States (1872) and of the American Chemical Society (1874). Original communications in chemistry were presented before the various philosophical societies, academies and institutes, and published in their *Transactions*, in the *Journal of the Franklin Institute* and, chiefly, in *Sillman's Journal*. With the appearance of the American Association for the Ad-

vancement of Science upon the scene (1848), the chemists rallied more and more strongly to its support until it had enrolled on its membership list a large number of the leading chemists of the country and its chemical section (Section C) was unquestionably the most powerful organization of chemists then in America.

MANUFACTURING CHEMISTS' ASSOCIATION OF THE UNITED STATES.

On May 29, 1872, the Manufacturing Chemists' Association of the United States was organized at the Astor House, New York City, Mr. Thomas S. Harrison, of Philadelphia, presiding. Manufacturers of chemicals whose annual product is at least $50,000 in value are eligible for membership. Its objects are to protect its members against unwise legislation and unjust freight discrimination, and to promote and aid any matter of general or special interest in the chemical industries. Its membership at present comprises forty-one representative corporations. Annual meetings are held in cities selected by vote. This brings me up to the founding of our own

AMERICAN CHEMICAL SOCIETY.

In the *American Chemist* for April, 1874, there was published a letter from Dr. H. C. Bolton, of Columbia College, entitled: "Centennial of Chemistry, 1774–1874," in which he referred to the many notable chemical discoveries of the year 1774, as the fruit of the labors of such men as Scheele, Lavoisier, Priestley, Cadet, Bergmann, and others. As the discovery of oxygen by Dr. Joseph Priestley on August 1, 1774, resulted in the overthrow of the Phlogistonists and the establishment of chemistry on its present basis, the writer points out that the year 1774 may well be regarded as the birth year of modern chemistry, and suggests that it "would be an agreeable event if American chemists should meet on the first day of August 1874, at some pleasant watering-place, to discuss chemical questions, especially the wonderfully rapid progress of chemical science in the past one hundred years." This suggestion met with the hearty approval of the editors of the *American Chemist* and they requested all chemists interested in the matter to send in their views at once. Among other letters, one was received from Miss Rachel L. Bodley, Professor of Chemistry at the Woman's Medical College, of Pennsylvania, which contained the following: "I made a pilgrimage last August to the grave of Priestley in Northumberland, Pennsylvania, and was deeply impressed by the locality, its associations, and its charming surroundings. My proposition is, therefore, that the centennial gathering be around this grave, and that the meetings, other than the open air one on the cemetery hilltop, be in the quaint little church built by Priestley, where might be exhibited the apparatus devised by the great scientist and used in his memorable experiments."

At a meeting of the Chemical Section of the New York Lyceum of Natural History, May 11, 1874, on motion of Dr. H. C. Bolton, the following resolutions were adopted: "WHEREAS, the discovery of oxygen by Priestley on August 1, 1774, was a momentous and significant event in the history of chemistry, being the immediate forerunner of Lavoisier's generalizations on which are based the principles of modern chemical science; and, WHEREAS, a public recognition of the one hundredth anniversary of this brilliant discovery is both proper and eminently desirable; and WHEREAS, a social reunion of American chemists for the mutual exchange of ideas and observations would promote good fellowship in the brotherhood of chemists; therefore, RESOLVED, that a committee of five be appointed by the Chair, whose duty it shall be to correspond with the chemists of the country with a view to securing the observance of a centennial anniversary of chemistry during the year 1874." The committee appointed consisted of Messrs. Bolton, Chandler, Wurtz, Leeds and Seeley. The suggestion of Miss Bodley that the meeting be held at Northumberland met with general approval, and the above committee having made all necessary preparations, issued the call, with the result that the chemists of the country assembled at Northumberland on July 31, 1874, where they were received and most hospitably entertained by the direct descendants of Priestley. Altogether about eighty chemists attended the celebration. The first session was held in the Public School building and Professor C. F. Chandler was chosen president. Various historical addresses were presented and congratulatory cablegrams exchanged with the chemists of Birmingham who were to unveil a statue to Priestley the following day. Some of Priestley's original letters were read, and a memorial address by Henry Coppee, LL.D., president of Lehigh University, was delivered at the grave.

At the afternoon session on July 31st, Professor Persifor Frazer "proposed the formation of a chemical society which should date its origin from this centennial celebration," since America had "not a single society to represent the chemical thought of the country." This was opposed by Professor J. Lawrence Smith, chiefly on the ground that there were "already two great organizations, the American Scientific Association (*sic*) and the American Academy of Sciences, which undertook to embrace in their proceedings everything connected with chemical research." Others expressing themselves as of similar opinion, it was finally resolved "that a committee of five be appointed from this meeting to coöperate with the American Association for the Advancement of Science at their next meeting, to the end of establishing a chemical section on a firmer basis." The committee appointed consisted of Messrs. Bolton, Silliman, Smith, Horsford and Hunt.

The attitude of Dr. J. Lawrence Smith towards the question will be

etter understood when it is recalled that he was president of the Ameri-
an Association for the Advancement of Science two years before (1872).
.t the Portland meeting of this Association the following year (1873), a
eparate heading in the physics section was given for chemistry and more
apers (six) were presented in that science than there had been in both
hysics and chemistry (five) the year before. At the close of the meet-
ıg, an informal gathering of chemists was held (August 26), with Professor
. A. Lattimore as chairman, at which resolutions were adopted asking
ɔr the organization of a chemical sub-section of the Association. These
esolutions were favorably received, and the chemists of the Association,
oöperating with the committee appointed at the Northumberland cele-
ration, organized a chemical sub-section at the Hartford meeting, August
7, 1874. As already stated, in the year 1882 this became a section, with
Dr. Bolton as its first chairman.

The formation of a chemical sub-section by the American Association
ɔr the Advancement of Science did not, however, fully satisfy many of
ıose who were present at Northumberland. These chemists felt that
'hat was needed was an independent American chemical society, which
hould unite in one active, aggressive organization the chemists of the
ountry, and that only through such an organization could the progress of
hemistry be properly stimulated and hastened. This need was felt most
eenly in New York City, and led finally to a meeting on January 22,
876, at the home of Dr. C. F. Chandler, at which a committee was ap-
ointed, consisting of Messrs. Chandler, Habirshaw, Endemann, Alsberg,
Iorton, Walz, Hoffmann and Casamajor, to attend to the preliminaries
f organization. A circular was prepared and mailed to about one hun-
red chemists residing in the vicinity of New York City, suggesting the
ɔrmation of a chemical society in New York. The replies were so
umerous (forty) and encouraging that it was decided to attempt the
ɔrmation of a national instead of a purely local society, and a circular
'tter was sent out to chemists in all parts of the country. Sixty chemists
utside of New York City signified their desire to join. The first meeting
ɔr organization was held April 6, 1876, at the New York College of
harmacy, with Dr. Chandler as Chairman, Isidor Walz as Secretary, and
hirty-five chemists in attendance. Drs. Bolton and Egleston both
hought the time inopportune for such a movement, as both the New
'ork Academy of Sciences and the American Association for the Ad-
ancement of Science had chemical sections. Nevertheless organization
'as proceeded with, a constitution and by-laws adopted, and at an ad-
ɔurned meeting, April 20th, Dr. John W. Draper was elected president.
'he first regular meeting after organization was held May 4, 1876, with
'ice-President Chandler in the Chair, thirty members and fifteen visitors
eing present. The first paper read was "On the Determination of the

Relative Effectiveness of Disinfectants," by Dr. H. Endemann. Arrangements were made with the editors of the *American Chemist* to publish the Proceedings of the Society and to supply the members with reprints.

On June 16, 1876, the Society gave a dinner at the Union League Club of Philadelphia, to the foreign chemists officially connected with the Centennial Exposition, which was attended by about seventy chemists.

On November 16, 1876, in Chickering Hall, New York City, Dr. Draper delivered his presidential address, on "Science in America," before a large and distinguished audience. At the close of the year, the membership of the Society was about 230. In November, 1876, the Society was incorporated in New York State. The first report of the librarian (Casamajor), published at the close of 1878, showed that the library then contained 344 volumes. On March 6, 1879, the publication of the *Journal of the American Chemical Society* began.

By the close of the year 1880, the Society was $900 in debt, with nominal assets in the shape of uncollected dues amounting to about $1,000. The publication of the *Journal* was therefore temporarily suspended and the debt liquidated by personal subscription. During this year there was frequently no quorum (fifteen) at the meetings. The *Journal* for 1881 (Vol. III) covered only 189 pages and contained twenty-seven original articles, eighteen of which were contributed by three authors, Leeds, Stebbins and Casamajor. In 1882, the lack of original material for the *Journal* appears to have been felt even more than the lack of funds. In 1884, it was found necessary to reduce the quorum from fifteen to ten. The *Journal* for 1888 (Vol. X) contained but ten original papers, and the following year the Society appeared almost moribund. There were but few papers submitted for the Journal and not enough money to publish even these. Personal subscriptions were again necessary to meet expenses. It was apparent to all that a radical change in policy was necessary or the organization would inevitably succumb. The fact that the Society was chartered in New York and all its meetings held in New York City, rendered the Society essentially a local one, in spite of the fact that the president and other officers were frequently selected from non-residents. The direct outcome of this condition of affairs was a steadily increasing discontent on the part of chemists in other parts of the country, resulting in a withdrawal of their interest and support, and the New York members, upon whom the burden was falling with ever-increasing severity, were rapidly becoming discouraged by this lack of support. As a natural corollary, there had begun a movement for the establishment of another chemical organization which should be more truly national.

At the meeting of Section C in Cleveland, in 1888, a committee was appointed on the formation of a national chemical organization. At the Toronto meeting, the next year (1889), this committee, after conferences

with committees appointed by the American Chemical Society, Association of Official Agricultural Chemists, Washington Chemical Society, and the Chemical Section of the Franklin Institute, recommended the establishment of a national organization. As the result of this report, the constitution of the American Chemical Society was revised so that an advisory council, local sections, and migratory meetings were authorized. The headquarters, however, remained in New York City. The first general meeting outside of New York was held at Newport, R. I., August 6–7, 1890, and was a great success. It was followed by the organization of the Rhode Island Section, the first of the local sections, which was duly chartered the following year. At the second general meeting, held in Philadelphia, December 30–31, 1890, a conference occurred of committees representing various chemical organizations to bring about consolidation, the basis of which was to be the union of all as the "American Chemical Society," the present New York organization to become a local section. At the third general meeting, at Washington, August 17–18, 1891, as the upshot of a similar conference of committees, it was resolved to unite on the above basis. The organizations represented at this conference were: The American Chemical Society (290 members), Section C of A. A. A. S. (200 members), Assoc. Official Agr. Chemists (75 members), Chemical Section of the Brooklyn Institute (75 members), Chemical Society of Washington (70 members), Chemical Section of the Franklin Institute (70 members), Chemical Society of the University of Michigan (60 members), Louisiana Sugar Chemists' Association (52 members), Cincinnati Chemical Society (29 members), and the Manufacturing Chemists' Association of the United States. A complete reorganization of the American Chemical Society followed, and a further revision of its constitution, and on April 29, 1892, the New York organization became the New York Section of the American Chemical Society. Just one month before this date, the "Chemical Society of Cincinnati and vicinity," organized December 19, 1890, was chartered as the Cincinnati Section. The Chemical Society of Washington, an organization of chemists working for the United States Government, and founded in 1884, became a local section the following year, retaining at the same time its original title. In 1893, Dr. Hart's *Journal of Analytical and Applied Chemistry* was consolidated with the *Journal of the American Chemical Society* and Dr. Hart appointed editor. The condition of our *Journal* at the time was not very encouraging, for when he took charge there were but two papers ready for publication, with five numbers of the *Journal* in arrears.

The seventh General Meeting occurred in this city (Chicago), August 21–26, 1893, in connection with the World's Chemical Congress of the Columbian Exposition. At the Buffalo meeting, August 21–22, 1896, the present plan of holding joint meetings with Section C of the American

Assoc. for the Advancement of Science was agreed upon. By its terms, the first two days are devoted to the American Chemical Society, with the exception of sufficient time on the first morning for Section C to organize and in the afternoon for the address of their vice-president, the rest of the meeting being then given up to Section C.

At the close of the year, 1897, the Society arranged with Dr. A. A. Noyes to take over the publication of the *Review of American Chemical Research*, and Vol. III of this *Review* was published with the 1897 *Journal*. The publication of abstracts and patents had been undertaken by the Society years before, beginning with Vol. I, No. 4, but it finally ceased with the January number of Vol. XVI (1893).

In 1902 associate membership was abolished. This attempted classification of our members was partly responsible for the separation from us of the industrial chemists and electrochemists.

The first recognition of the growing strength and importance of the various branches of chemistry was made in 1904 when the general meetings were for the first time held in sections.

This year, as you know, we have taken a great stride in advance by the successful publication of *Chemical Abstracts*, superseding the *Review of American Chemical Research*. In spite of the necessary increase in dues from $5.00 to $8.00, we are gaining new members more rapidly than ever. Within the past year three new local sections have been chartered, Syracuse, St. Louis and Wisconsin, and others are in process of formation.

It was hoped at the time the American Chemical Society was reorganized that all existing chemical societies would come into the fold and that the American Chemical Society would be the one organization to include all the chemists of the country. Unfortunately, this has not yet been realized. Not only did some of the chemical societies then existing fail to come in, but other separate and independent organizations have since arisen. A brief consideration of these is necessary to any proper understanding of existing conditions. I cannot, of course, take up those of purely local character, although some of them (for example, those at Detroit, Cleveland and elsewhere) are strong in numbers and influence. We hope that they will all ultimately form new local sections of our Society or unite with existing local sections. Nor is there time to take up the consideration of chemical sections of academies of science or of scientific institutes, although some of them exert a powerful influence locally (as the chemical section of the Franklin Institute, for example).

It is more important to consider those chemical societies which possess a more national character, pointing out the reasons for their establishment, the particular field covered, and their present strength in numbers and influence. The most important of the chemical organizations established

since the founding of the American Chemical Society, taking them up in chronological order, are as follows:

1880, Assoc. of Agricultural Chemists (later the Assoc. of Official Agricultural Chemists).

1894, New York Section, Society of Chemical Industry.

1898, New England Association of Chemistry Teachers.

1900, New York Section, Verein Deutscher Chemiker.

1902, American Electrochemical Society.

1904, Western Assoc. of Technical Chemists and Metallurgists.

1906, Society of Biological Chemists.

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

The condition of agricultural chemical work in the United States in 1880 has been described by Dr. Wiley as "chaotic." There was no unity of purpose, action or methods, no standard of comparison or reference. The great differences in analytical methods led to constant wrangling and litigation between buyer and seller.

It was to put an end to this state of affairs that the Hon. J. T. Henderson, Commissioner of Agriculture for Georgia, at the suggestion of Mr. H. J. Redding, issued a call for a convention of agricultural commissioners and chemists for the purpose of securing uniformity in analytical methods. This convention was held in Washington, July 28, 1880, with Judge Henderson as Chairman and A. R. Ledoux as Secretary, the chief topic considered being fertilizer analysis. It was further decided to form a division of the sub-section of chemistry in the American Association for the Advancement of Science and to hold the next meeting with this Association. This joint meeting occurred in Boston, August 27, 1880, and a committee of three was there appointed to secure the formation of a permanent chemical section in the American Association with agricultural chemistry as a sub-section. The third meeting of the Association, held in the room assigned to the chemical sub-section of the American Association, Cincinnati, August 18, 1881, transacted its business separately, but read its papers before the American Association.

After the Cincinnati meeting, the interest of agricultural chemists in collaboration seemed to die out, due apparently to the difficulty of harmonizing the conflicting interests of the trades chemists and official chemists. After the lapse of three years, Judge Henderson again called a meeting, which was held at Atlanta, Ga., May 15, 1884, and once more discussed the unification of analytical methods. At the next meeting, held in Philadelphia, September 8–9, 1884, in conjunction with the American Association, it was decided to form a separate and independent organization instead of a sub-section of the American Association, and on September 9th, the Association of Official Agricultural Chemists came into existence.

At the eleventh annual meeting, Washington, August 23, 1894, the Society of Leather Chemists was absorbed and a reporter on tannin appointed.

According to the constitution of this Association, its objects are (1) to secure uniformity and accuracy in the methods, results, and modes of statements of analysis of fertilizers, soils, cattle foods, dairy products, and other materials connected with agricultural industry; and (2) to afford opportunity for discussion of matters of interest to agricultural chemists. Its voting members must be analytical chemists connected with the U. S. Dept. Agriculture, or with any state or national agricultural experiment station or agricultural college, or with any state or national institution or body charged with official control of materials named in (1) above. Other analytical chemists are permitted to attend meetings and participate in the discussions but not to vote or offer motions. Referees are appointed to prepare and distribute samples and standard reagents and to tabulate and present results before the Association.

The adoption and publication of these "official methods" has brought order out of chaos. The results of the work of the Association are published by the Division of Chemistry, U. S. Dept. Agriculture.

There are no dues, as publication and postage are paid for by the Department of Agriculture, while samples are sent out by C. O. D. express.

Its membership is assumed to include all official chemists—State, Municipal and Federal.

At the recent Jamestown meeting of the Association, 90 members were present. The meetings are usually held in Washington, where the attendance is often double this number.

AMERICAN SECTIONS, SOCIETY OF CHEMICAL INDUSTRY.

The New York Section of this Society was founded May 2, 1894. Since then, New England and Canadian Sections have also been established. The present membership of the New York and New England Sections combined is about 1500. It is the chief organization of industrial chemists in the country, and its journal is the best known publication of its kind. Among the reasons for its establishment, as stated by one of its founders, are (1) that the meetings of the New York Section of the American Chemical Society were at the time devoid of interest to chemical manufacturers; (2) that the American Chemical Society itself did nothing to promote chemical industry; (3) that it discriminated against industrial articles submitted for publication; and (4) that manufacturers were admitted only as Associates.[1]

[1] It need hardly be said that these statements were based on an almost complete misapprehension of the attitude of the American Chemical Society toward Industrial Chemistry.

NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS.

Of quite a different type is the New England Association of Chemistry Teachers. Founded February 19, 1898, "to promote efficiency in the teaching of chemistry," this Association now has a membership of nearly 200. Any person interested in the teaching of chemistry is eligible to membership. The number of Active members is limited to 75, but no limit is set for the number of Associate or Honorary members. Three meetings a year are held, most of them occurring in the vicinity of Boston. The *Annual Report* of these meetings makes a volume of about 110 pages. Active members pay $2.00 a year, Associates $1.00. There are no local sections. The character of the permanent committees gives a good idea of the scope of the work. They are as follows: College requirements, current events and publications, high school course of study, industrial chemistry, laboratory construction, new apparatus, instruction, and social committee.

NEW YORK SECTION, VEREIN DEUTSCHER CHEMIKER.

Established in December, 1900, this New York Section has at present 125 members. Its meetings are generally held at the Chemists' Club in New York City, at the close of those of the New York Section of the Society of Chemical Industry, and are purely social in character. The official publication of the Verein is the *Zeitschrift für angewandte Chemie.*

AMERICAN ELECTROCHEMICAL SOCIETY.

The original call for the organization of this society was dated Philadelphia, October 19, 1901, and was sent to about thirty people. It was signed by Messrs. Hering, Reed, Richards, Roeber, Sadtler and Wahl, and began thus: "The rapidly growing importance of the subject of electrochemistry, and the want of suitable occasions in this country for the discussion of papers and questions pertaining thereto by those especially interested, have suggested the advisability of founding a national Electrochemical Society, similar in its organization to the American Chemical Society and the American Institute of Electrical Engineers."

The preliminary meeting was held at the Engineers' Club, Philadelphia, and it was decided to organize, provided seventy-five members were assured. A second circular letter was therefore sent out to engineers, chemists and metallurgists, including all members of the American Chemical Society and of the American Institute of Electrical Engineers. This was dated New York, November 25, 1901, and contained the following: "The products of electrochemical industries in this country at the present time amount to about one hundred million dollars per year. The growing importance of these industries and the fact that scientists and engineers interested in electrochemistry are now distributed among at least half a dozen different societies, and therefore have no common

medium of communication, suggested the formation of an American Electrochemical Society, on the same general plan as the American Chemical Society and the American Institute of Electrical Engineers..... The bringing together in this way of those engaged in the scientific study of electrochemistry and the practical engineers and pioneers of the industry, will be of inestimable value to both."

It is appropriate to add that one of the most prominent of the charter members states that one of the reasons for forming a separate society was that electrical engineers interested in chemistry were, at that time, admitted by the American Chemical Society only as associates.

The meeting for organization took place at the Manufacturers' Club, Philadelphia, April 3, 1902, fifty-two members being present. The total number of charter members was 336.

Two volumes of *Transactions* are published annually, and three local sections have been formed: New York, Philadelphia and Madison (Wis.). The total membership at present is about 700.

WESTERN ASSOCIATION OF TECHNICAL CHEMISTS AND METALLURGISTS.

In 1904 this Association appeared on the scene. It was established because, in the opinion of its organizers, there was then no society in the country that met the needs of the men engaged in the extraction of metals and rare earths from their ores. It is incorporated under the laws of Colorado, with headquarters at Denver.

Its first general annual meeting was held at Denver, Colo., the second at Salt Lake City, and the third is now being held at Deadwood, S. D. Local sections have been established at Denver, Salt Lake City and Butte, and others are in process of formation. The total membership at present is about 250. The objects of the Association are the general advancement of technical chemistry, the improving and promoting uniformity in methods of metallurgical analysis and assaying, and the encouragement of research in the metallurgy of precious and rare metals. Any one interested in these objects is eligible for membership. The official organ of the Association is the *Western Chemist and Metallurgist.*

SOCIETY OF BIOLOGICAL CHEMISTS.

The latest separate chemical society is that of the biological chemists.

In 1899 a number of New York physiological chemists established the Society of Physiological Chemists. This is a purely local organization, meeting about once a month during the winter for the presentation and discussion of recent important work in this field. It is somewhat of the nature of a seminar in physiological chemistry, abstracts and reviews being submitted rather than original contributions.

The growth of this Society of Physiological Chemists, the development of the Biochemical Section of the American Chemical Society (established

), the increasing number of chemical papers on the programmes of the rican Physiological Society and the great success of the recently blished *Journal of Biological Chemistry*, "were among the influences stimulated thoughts of a national organization of biochemical work-

the meeting for organization, New York City, December 26, 1906, twenty-nine biological chemists present were addressed by Professor as follows: "We have become convinced that there is need in this try for an organization which shall further the interests and foster growth of biological chemistry. Biological chemists at present are ated with widely different societies and come little in contact with the : body of men who are interested in biochemical work. Whether we emists have as our field of work the physiological chemistry of our cal schools, or deal with the chemical problems of botany, zoology, ology, pharmacology, or medicine, we all have one common meet-round, and that is, chemistry as applied to animal or vegetable struc-, living or dead. As distinguished from the work of pure chemists, nic or inorganic, our efforts are directed towards throwing light on life processes and functions of living structures, with the help of ical and physico-chemical methods..... Organization develops lination of effort, encourages research, it furnishes the mechanism competent criticism and helpful discussion and .... . makes it ent to faculties of science and medicine, and to scientific and medical ties, that a great and growing department of research demands its g place in the general scheme of higher education. . . .I believe we can have a society on broader lines than is possible to a mere on. We wish to draw into our society biological chemists in all de-nents of biology, including those organic and physical chemists who a lively interest in our subject."

ghty-one chemists enrolled as charter members. Their contributions ublished mainly in the *Journal of Biological Chemistry*, which I under-l, is not an official organ, but the private property of Messrs. Abel Herter.

the limited time available, I have endeavored to give you some idea e more prominent American chemical societies of the past as well as e present, the reasons for their establishment, the fields covered, data indicating their present size and influence.

en this hasty and imperfect survey unavoidably forces upon us the lusion that, in the judgment of many of the chemists in the country, American Chemical Society has not adequately met the needs in all ches of the work, otherwise these separate societies would not have n. Such a condition of affairs must, of course, cease, or total dis-ration will only be a question of time.

I am happy to say that the Society is fully alive to the situation and that a larger future seems opening up before us. The first step in this direction has been taken—the publication of *Chemical Abstracts*. It might justly be called a stride rather than a step, for, in my opinion, no single act on the part of our Society could have done more to unite the chemists of the country than the publication of these abstracts, covering as they do every branch of the subject.

Any national organization of chemists, if it would be successful, must take into account the following factors:

I. Specialization.
II. Publication.
III. Geographical location.

I. *Specialization.*—The history of chemical organization shows the usual evolution from the general to the special. First came the societies for science in general, then those devoted to chemistry alone, and now those for special branches, which, in their turn, may undergo a still further division in the years to come.

Every chemist has some one branch of the subject in which he is particularly interested. But little progress would be recorded were it not so. It is as fitting as it is inevitable, that those following the same specialty should wish to meet together periodically to discuss matters of mutual interest. It is equally certain that as they grow in numbers they will seek organization, and demand a medium of publication which shall give suitable recognition of the importance of their special branch of chemistry. The society which fails to take cognizance of the growing strength of specialization and to lay its course accordingly, fails to grasp its opportunities and slowly but surely will be crowded to the wall. We should not labor under the delusion that if our society fails to recognize this tendency to specialize, specialization will therefore cease.

The vital point is that the American Chemical Society must show that it can adapt itself to this condition, and by suitable changes in its plan of organization do far more for the fostering and stimulating of special branches of chemistry than could be accomplished by separate and independent societies. That this can and will be demonstrated, I confidently believe, and I am sure that every well-considered move in this direction will meet with the hearty approval of all.

The practice of holding our semi-annual meetings in sections is a move along this line, and I believe that a further advance would be the organization of these sections on a somewhat different basis. As a first step, they might elect their own officers to serve for a year, let us say, who shall do what they can to make the semi-annual meetings as successful as possible, by providing attractive programmes and a large attendance, inducing other organizations with similar interests to meet with

them (as the Society of Biological Chemists is now meeting with our Biological Section), pointing out to the Council in what ways the Society may be made more valuable to their particular group of members, and in general, doing whatever they can to stir up increased interest. These general sections should be given as large a measure of self-government as possible. Their presiding officers should be *ex-officio* members of the Council, and should be associated with the president and secretary in the preparation of the programmes for the general meetings. This is essentially the policy recommended in 1903 by the committee of which Dr. A. A. Noyes was chairman, and it is not unlikely that such a policy, particularly when accompanied by a suitable development of our publications, would lead some of the existing specialized societies to unite with us.

To those of our members who fear that such a move may introduce a disintegrating element, I would cite the recent action of the Verein Deutscher Chemiker.

This great German society, at its recent general meeting in Danzig, May 23–25, 1907, changed its constitution and by-laws so as to provide for the establishment of separate sections or groups (Fachgruppe) for those working in the same field.

So far, sections have been organized for Paper Chemistry, Fermentation, and Technological Chemical Instruction, and the following additional ones are contemplated in the immediate future: Heavy Inorganic Chemicals, Legal Protection of the Trade, Color Chemistry, Medico-pharmaceutical Chemistry, Analytical, Organic, Photo- and Electrochemistry, and Chemical Apparatus and Machinery. Calls have already been issued for the organization of several of these.

At the preliminary meeting for the organization of the Fermentation Section, in Berlin, the 11th of last November, Geheimrath Delbrück, in the course of his opening remarks, said: "that in the profession there is great need for the founding of such a section, is shown by the large attendance at this meeting and the numerous applications for membership." He stated further that 66 chemists had already signified their desire to join and that "there would thus be added to the Verein a whole group of new members." Some of those present even thought it wise to prepare for the formation of sub-sections within the sections.

To any one reading in the *Zeitschrift für angewandte Chemie* the reports of their meetings, it will appear that a wave of enthusiasm is sweeping all along the line as the direct result of this plan of establishing sections. Not only have the members no doubts whatever as to the beneficial effects of such a sub-division of the Verein, but they appear confident that it means a brighter future and a wider sphere of usefulness for their organization.

II. *Publication.*—The publications of the Society must truly represent the varied interests of the membership. To those of our number who are situated at a considerable distance from any large city and have no library accessible and no local section, the character of our publications is of preëminent importance. The development of specialization already alluded to must be provided for either (1) by the establishment of separate journals by our Society to more fully cover these special fields, or (2) by the development of appropriate divisions within our present *Journal.*

Under the former plan, some such division as the following might be suggested, although probably no two men would divide up the field in exactly the same way:

(1) Our present *Journal*, to contain articles of general interest, reviews, proceedings, and the like, as well as articles in those branches for which no special journal is provided.

(2) *Chemical Abstracts.* A publication needed by every chemist, no matter what his specialty, and a most valuable bond, therefore, in holding all chemists together.

(3) *A Journal of Industrial and Engineering Chemistry*, to include the best features of the existing journals of industrial and engineering chemistry and metallurgy.

(4) *A Journal of Biochemistry.* If consolidation with the Society of Biological Chemists could be brought about, the present *Journal of Biological Chemistry* might become the official organ.

(5) *A Journal of Inorganic and Physical Chemistry*, to include the present *Journal of Physical Chemistry*, or to be a continuation thereof. There is very good reason for believing that this can be brought about when the time seems opportune.

(6) *A Journal of Organic Chemistry.* If a way could be found acceptable to Dr. Remsen, by which the present *American Chemical Journal* would take this place, the problem would be a much simpler one.

Of these various journals, all the members would receive the first two, while the others would be furnished at a price slightly in excess of the actual cost—a price, by the way, far below that for which separate societies could afford to supply them. Or perhaps, some different arrangement would be deemed preferable.

The other plan contemplates segregation rather than separation, and has in mind the development of our present *Journal* until it somewhat resembles a union under one cover of all the various journals mentioned above, with the possible exception of *Chemical Abstracts.*

This latter plan has in its favor evident advantages. It would cost far less for publication, and such an enlarged *Journal* could probably be sent to all the members without any additional charge whatever. Uncertainties as to the proper place for an article to appear would arise only

as between subdivisions of one and the same journal, and not as between different journals. Repetition could be avoided by proper cross-references. There would never be any very great danger of a lack of sufficient material for such a journal. Its large circulation would also make it a most desirable medium for advertising, and the increased income from this source would still further reduce the cost of publication.

Perhaps the chief objection to such a plan lies in the rapidly increasing amount of material submitted to our various chemical journals. The bulk of this material if not already too great to be handled properly by any one journal, would certainly become so in the course of the next few years.

It may be that a combination of these two plans would appear best, arranging for the issuing of those separate journals which seem most urgently needed at the present time, if there are any such, and meanwhile developing the journal by a segregation of its contents, perhaps with suitable divisional headings, so that when the moment is most opportune these sub-divisions may start an independent career as special journals.

Already an able and energetic committee is at work on the question of the advisability of our publishing a *Journal of Industrial and Engineering Chemistry*, and we hope to have a report from them at this meeting.[1]

III. *Location.*—As far as practicable, opportunities should be provided for our members in all parts of the country to hold periodic meetings. To insure this we have our Local Sections and migratory General Meetings. So far as the latter are concerned, however, the country is so large and our membership so widely scattered, that only a small proportion find it possible to attend. It might be wise, therefore, to hold one general meeting during the Christmas holidays, and during the summer have several separate gatherings in different parts of the country—say, one West of the Rockies and two or more in the East.

To return to my original statement, what the American Chemical Society needs is the enthusiastic and intelligent coöperation of its members. I am sure that the enthusiasm will be forthcoming, and I trust that the data presented may be of some service in helping you to decide intelligently as to the best plans for the development of our Society.

THE BROMATES OF THE RARE EARTHS.

Part I. A New Method for the Separation of the Yttrium Earths.

By C. James.

Received December 6, 1907.

During recent years chemists investigating the rare earths have di-

[1] The report will be found in Proceedings of this number.

rected their efforts more towards the cerium group than towards the yttrium earths, with the result that the elements cerium, lanthanum, praseodymium, neodymium, samarium, europium and gadolinium are fairly well known. On the other hand, the yttrium earths, with the exception of yttrium, ytterbium and scandium are still but poorly defined. Many investigators have been of the opinion that "new" erbium is complex, while almost nothing is known about thulium, holmium, dysprosium and terbium. In addition to the above, victorium, announced by Crookes, is believed by Urbain and some others to be a mixture, although its discoverer still claims that it is a separate and new, individual element.

In the case of the cerium group, several excellent methods of fractional crystallization have been developed. On the other hand, no rapid and simple method has been applied to the yttrium earths with the possible exception of the method of Urbain, using the ethyl sulphates, and some methods employing compounds of a costly nature, such as the acetylacetonates and the metanitrobenzenesulphonates. As one must deal with many kilograms of material, expensive compounds are out of the question unless the separation should prove almost quantitative, which is never the case.

Urbain's ethyl sulphate method[1] gives good results. He says that yttrium, neoerbium and ytterbium accumulate in the most soluble portions, with no trace of the lanthanum group and no earths of the samarium and gadolinium groups. It is very difficult to obtain erbium from fractions rich in holmium by its use and for separating earths of the same group, the method of fusing the nitrates is still the best. Another difficulty is due to the fact that the ethyl sulphates are inclined to hydrolyze unless special precautions are taken.

The fractionation of the simple nitrates from concentrated nitric acid proposed by Demarcay[2] is very tedious and the use of a solvent of such a character causes great inconvenience in the laboratory.

The separation obtained by taking advantage of the difference of solubility of the oxalates in a saturated solution of ammonium oxalate, developed by Carl Auer von Welsbach,[3] gives interesting results. It has drawbacks, however, as it involves the use of two temperatures and requires a large number of operations.

Among the remaining methods only a few need be mentioned: Fusion of the nitrates and separation of the most easily decomposed portions by their insolubility in water, separates ytterbium and scandium at one end, and yttrium and terbium at the other. To obtain ytterbium free

[1] Compt. rend., 126, 835; 127, 107; 132, 136.
[2] *Ibid.*, 122, 728; 130, 1020.
[3] Monatsh., 27, 935.

from erbium and thulium, requires about seventy operations. It is also extremely difficult to get yttrium pure by this method, since terbium clings.

Fractional precipitation of the concentrated neutral nitrate solution by means of magnesium oxide,[1] tending to throw down the less basic elements first, gives similar results.

The preparation of pure yttria by Muthman and Bohm's chromate method[2] is comparatively simple, but unfortunately it is of no value for separating the other members.

The fractionation obtained by boiling a solution of the oxalates in ammonium carbonate[3] works well for obtaining erbium free from holmium and dysprosium, on the one side, and thulium, ytterbium and scandium on the other.

Fractional precipitation to be of value must be very rapid. Fractional crystallization is to be preferred, for it is much easier to carry out a large number of operations. As a rule, in fractional precipitation methods, especially where dilute solutions are employed, a good deal, if not most, of the material is washed away. It is highly desirable, therefore, that a method consisting of fractional crystallization of some type of isomorphous compounds, with greatly varying solubilites, should be found. With this object in view, the author has examined the sulphites, xanthates, succinates, double carbonates with sodium glycollates, methyl sulphates, normal propyl sulphates, camphorates, iodates, thiocyanates, monochloracetates, monobromsuccinates, oleates, bromates, etc., besides nearly every compound proposed in literature for the purpose of fractionation. The bromates are the best suited for the purpose of all those examined up to the present time.

The bromates are easily prepared by using barium bromate, which, in turn, is formed by mixing boiling solutions containing the required amounts of barium chloride and potassium bromate. Because barium bromate is not very soluble even in boiling water, it is highly important that the precipitate should be finely divided, otherwise the double decomposition between the rare earth sulphate and barium bromate will take considerable time. The formation of large crystals is prevented by rapidly cooling the mixed boiling solutions. As potassium bromate can be prepared cheaply, the rare earth bromates are not costly to obtain.

The rare earth material, generally in the form of the oxalates, is mixed into a paste with sulphuric acid and the temperature raised until the fumes of sulphuric acid cease to be evolved. The residue is then finely powdered, dissolved in ice-cold water, and the resulting solution poured

[1] Muthman and Rolig, Ber., 31, 1718.
[2] Ber., 33, 49; Chem. News, 81, 169.
[3] This Journal, 29, 495; Chem. News, 95, 181.

over an excess of barium bromate. This operation is best carried out in a large evaporating dish placed on the water-bath, care being taken to keep the mass well stirred.

After a time the precipitate is allowed to settle and some of the clear liquid taken up by means of a pipette and added to a warm solution of barium bromate; if no precipitate is obtained the liquid is filtered off. Sometimes, however, a precipitate is formed which consists of barium bromate and, therefore, it is best to dilute with water and boil. If the precipitate persists, either more stirring or more barium bromate is required.

When the double decomposition is complete a little bromine is often liberated, but there is not sufficient to cause any inconvenience in the laboratory. This is evidently due to the fact that a small amount of bromic acid is formed by the action of a trace of free sulphuric acid accompanying the rare earth sulphates. The latter should, therefore, be well ignited.

The filtered liquid is evaporated until a drop, removed on the end of a glass rod, nearly solidifies when stirred on a watch glass. Under these conditions just about half of the substance in solution crystallizes out on cooling. After a little experience there is absolutely no difficulty in judging the most convenient concentration. If the fractionation is carried out in porcelain dishes a little water should be sprayed on the surface so as to prevent the top from solidifying to a crystalline mass.

Casseroles are by far the best utensils to use for this work, especially if small amounts of substances are being separated, as they can be covered by large watch glasses. This prevents rapid crystallization and the tendency of the material to creep up the sides of the vessel. Also there is no need to spray any water on the surface after evaporating or dissolving. Very often, but usually when working with small quantities, the liquid refuses to crystallize or else the crystals separate out as a fine feathery mass, so that it is quite impossible to pour off the mother liquor. If it does not crystallize, the best procedure is to add a trace of the solid, when the whole immediately solidifies, forming the feathery type of crystals as mentioned above. The mass is then carefully heated so as to dissolve all but a very little, which will start the crystallization as the liquid cools. An even better plan is to commence the operation by the addition of a crystal while the liquid is still quite hot.

When working on the large scale, very fine hexagonal prisms are often obtained, some being more than two inches in length and over a quarter of an inch in thickness.

Even after six series of crystallizations a considerable change is easily apparent, although this is shown more by the spectroscope than by the color. The most soluble fraction is very pink and it gives an intense

rbium spectrum. The thulium red is also very strong and the band ı the blue has made its appearance while the bands of holmium and ysprosium have nearly disappeared. The least soluble fraction is still inkish and gives intense dysprosium and holmium bands and a weak rbium spectrum. The color of the oxide of this fraction is orange, ıowing that terbium accumulates at this end. After the process has een continued until some twenty fractions have been obtained, the ast soluble portion forms brilliant colorless crystals, which dissolve ı water with a tinge of greenish yellow color, seen only in concentrated olution. The absorption spectrum of this fraction shows very faint ımarium and holmium bands, while those of dysprosium are much ronger. Practically the whole of this fraction consists of an earth giving colorless salt, yttrium. And as the oxide is of a brown ochre color it ıows that terbium collects in the least soluble portion. As one goes own the series, the fractions become yellower and the oxides paler. In ıe fractions that show the strongest yellow, the dysprosium and holmium ands are very intense, and the oxide becomes yellowish. Farther along ıe series, the lines of erbium make their appearance and even while the rbium absorption is still weak the liquid assumes a pink color. This ıcreases until it reaches a rosy pink, at which stage the spectroscope ıows only erbium bands, and the oxide is of a pure rose tint. Further on till the thulium band in the red shows itself, while the solutions become aler and give a very stong thulium spectrum, the erbium bands becomıg decidedly weaker. The most soluble fraction is reached when the olution is nearly colorless, the erbium spectrum is faint, while that of ıulium, although fainter, is still intense. The oxide of this last fraction white and dense and consists largely of ytterbium.

The above series show that the rare earth bromates arrange themelves in the following order of solubility:

Samarium (Europium?, Gadolinium?), Terbium, Yttrium, Dysproum, Holmium, Erbium, Thulium and Ytterbium—which is similar to ıe solubilities of the oxalates in ammonium oxalate, but different from ıe ethyl sulphates; since according to Urbain, yttrium, erbium and ytterium ethyl sulphates are found in the most soluble portion.

A fair conclusion can be drawn that the use of the ethyl sulphate method ould prove valuable in conjunction with the bromate, especially for ıe separation of yttrium from dysprosium and holmium and perhaps or the separation of thulium from ytterbium.

Finally, the author would like to point out some of the rapid separaons obtained by this method, the most remarkable being the sepaıtion of thulium from erbium. And since ytterbium is still more solule than thulium, its removal is even easier. For example, erbium ıaterial, supposed to be quite free from thulium, was converted into

the bromate and crystallized four times, when the most soluble portion gave the thulium spectrum.

Dysprosium and holmium also separate from erbium with comparative ease, and as yttrium places itself between terbium and dysprosium, the latter element can be obtained terbium-free. The division between dysprosium and holmium is not so marked.

The absorption spectra and the colors of the various fractions show curious changes which are not altogether understood and may be simply due to the comparatively small amount of material under examination.

More material (15 kilos) is at present being fractionated and in the near future the less basic portion of earths derived from about 100 kilos of euxenite and 100 kilos of yttrotitanite, etc., will also be included. The bromate method will be further investigated and also applied to the cerium group and the results published at an early date.

NEW HAMPSHIRE COLLEGE,
Durham, N. H., November 18, 1907.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF LEAD.

Preliminary Paper—The Analysis of Lead Chloride.

GREGORY PAUL BAXTER AND JOHN HUNT WILSON.

Received December 2, 1907.

Although lead is one of the most common elements, its atomic weight has received comparatively little attention, the value at present accepted being based almost wholly upon the work of Stas.[1] Of the earlier determinations of this constant those of Döbereiner[2] and Longchamps[3] can hardly be considered as possessing other than historic interest. The first results which can lay claim to accuracy are those of Berzelius,[4] who obtained values ranging from 206.7 to 207.3 by reduction of litharge in a current of hydrogen. Berzelius also synthesized the sulphate from metallic lead with the result 207.0.[5] Shortly after, Turner[6] criticized

[1] Earlier work on the atomic weight of lead has been carefully summarized by Clarke. Smithsonian Miscellaneous Collections, Constants of Nature, "A Recalculation of the Atomic Weights," 1897.

In recalculating the data of earlier determinations the following atomic weights have been used in this paper:

$$O=16.000;\ Ag=107.88;\ Cl=35.46;\ N=14.01;\ S=32.07$$

Richards and Wells, Pub. Car. Inst., No. 28 (1905); Richards and Forbes, *Ibid.*, No. 69, p. 47 (1907); Richards and Jones, *Ibid.*, No. 69, p. 69; Report of International Committe on Atomic Weights, This Journal, 29, 110 (1907).

[2] Schweig. J., 17, 241 (1816).

[3] Ann. chim. phys., 34, 105 (1827).

[4] Pogg. Ann., 19, 314 (1830).

[5] Lehrbuch, 5th ed., 3, 1187 (1845).

[6] Phil. Trans., 527 (1833).

the first method employed by Berzelius and attributed the irregularity of his results to the action of lead oxide on the siliceous matter of the tube at the temperature employed in the reduction. By the conversion of both the metal and the oxide into sulphate Turner, in a painstaking research, deduced the values 207.0 and 207.6 respectively, and by converting the nitrate into sulphate, 204.2. Marignac[1] converted metallic lead into the chloride by heating in a stream of chlorine and obtained the result 207.42. Both Marignac[2] and Dumas[3] analyzed lead chloride. Marignac, who dried the salt at 200°, by titration against silver found the atomic weight of lead to be 206.81, and from the ratio of lead chloride to silver chloride, 206.85. Dumas subsequently showed that lead chloride, even when dried at 250°, retains moisture and is somewhat basic, and in one analysis in which corrections are applied for these errors, found a somewhat higher value, 207.07, as was to be expected. Chloride analyses by early investigators are, however, to be universally distrusted, owing to neglect of the very considerable solubility of silver chloride, thus producing too low results.

Stas's[4] work upon the syntheses of lead nitrate and sulphate from the metal is undoubtedly the most accurate contribution upon the subject, although a careful consideration of his work discloses minor defects, many of which he recognized himself. The metallic lead used in the syntheses was finally fused under potassium cyanide. Whether or not this treatment introduced impurities into the metal is uncertain. Stas himself suspected the presence of alkalies in the metal. Since the nitrate could not be dried above 150° without decomposition, it undoubtedly contained moisture, and Stas calls attention to this point. The sulphate was made by treatment of lead nitrate, resulting from the nitrate syntheses, with sulphuric acid. The sulphate was dried finally at dull redness, and was probably free, or nearly free, from moisture, although it may have contained traces of lead oxide resulting from occluded nitrate, as well as sulphuric acid. Most of these probable errors tend to lower the observed atomic weight, so that Stas's value from the series of nitrate syntheses, 206.81, and that from the sulphate series, 206.92, are to be regarded as minimum values. The reader of Stas's own account of his work upon lead cannot fail to be impressed with the fact that he was somewhat dissatisfied with the outcome of his research. Mention should also be made of the work of Anderson and Svanberg[5] on the conversion of lead nitrate into oxide, although the method was

[1] Ann., 59, 289 (1846).
[2] J. pr. Chem., 74, 218 (1858).
[3] Ann., 113, 35 (1860).
[4] Œuvres Completes, 1, 383.
[5] Ann. chim. phys. [3], 9, 254 (1843).

primarily employed in an endeavor to fix the atomic weight of nitrogen. Their results yield the value 207.37.

The discrepancies between the results of these various experiments only serve to emphasize the need of a redetermination of the value in question, and it was with this object in view that the work embodied in this paper was undertaken.

The search for a suitable method for determining the atomic weight of lead failed to reveal any more promising line of attack than those already employed for the purpose. With an element of so high an atomic weight as lead, in any method involving the change of one of its compounds into another, errors which may be insignificant with elements of small atomic weight are magnified in the calculations to undesirable proportions. Furthermore, during the following investigation, reduction of the chloride and oxide in hydrogen was investigated far enough to show that complete reduction of either compound was extremely difficult, if not impossible, without loss of material from the containing vessel by sublimation, aside from the fact that all available material for containing vessels is acted upon by either the fused salt or the reduced metal. The elimination of moisture from lead nitrate or lead sulphate without decomposition of the salts seemed likely to prove a stumbling block in the use of these substances. Finally, in spite of the slight solubility of lead chloride, the determination of the chlorine in this salt by precipitation with silver nitrate was chosen as presenting fewest difficulties. In the first place, the determination of a halogen can be effected with great accuracy. In the second place, the elimination of moisture from lead chloride is an easy matter, since the salt may be fused in a platinum vessel in a current of hydrochloric acid gas without attacking the platinum in the least and without the production of basic salts. In the third place, silver chloride, which has been precipitated from a dilute solution of lead chloride by means of silver nitrate, does not contain an amount of occluded lead salt large enough to be detected.

Purification of Materials.

Water.—All of the water used in either the purification or the analyses was distilled twice, once from an alkaline permanganate solution and once from very dilute sulphuric acid. Block-tin condensers were used in both distillations, and rubber and cork connections were avoided. Generally, receivers of Jena glass were employed, but in certain cases the water was collected in platinum or quartz vessels.

Hydrochloric acid.—Commercial C. P. hydrochloric acid was diluted with an equal volume of water and distilled with a quartz condenser, only the middle fraction being collected.

Nitric acid.—Nitric acid was distilled with a platinum condenser,

ntil free from chlorine. Two distillations were invariably sufficient o accomplish this end, if the first third of each distillate was rejected.

Silver.—Pure silver was obtained by methods already many times mployed in this laboratory. Silver nitrate was dissolved in a large olume of water and the silver was precipitated as chloride with an exess of hydrochloric acid. The precipitate was thoroughly washed nd reduced with alkaline invert sugar. The reduced silver, after being vashed, was dried and fused on charcoal in the flame of a clean blast amp. After the buttons had been cleaned by scrubbing with sand nd etching with nitric acid, they were dissolved in pure dilute nitric cid and the silver was precipitated as metal with ammonium formate.[1] his silver was washed and fused in the flame of a blast lamp on a crucible f the purest lime. The buttons were cleaned as before, and then elecrolyzed.[2] Finally the electrolytic crystals were fused in a boat of the urest lime in a porcelain tube in a current of pure electrolytic hydrogen.[3] he bars of silver were cut in pieces with a fine steel saw, etched with ilute nitric acid until free from iron, washed, dried, and heated in a acuum to 400°. The silver was kept in a desiccator containing solid otassium hydroxide.

Lead chloride.—Three samples of lead chloride from two entirely diferent sources were employed. Sample A was prepared from metallic ead. Commercial lead was dissolved in dilute nitric acid, and the soution, after filtration, was precipitated with a slight excess of sulphuric cid. The lead sulphate was thoroughly washed, suspended in water, nd hydrogen sulphide was passed in until the sulphate was almost comletely converted into sulphide. Next, the sulphide was washed with vater, dissolved in hot, dilute nitric acid, and the solution was freed rom sulphur and unchanged sulphate by filtration. The lead nitrate hus obtained was crystallized twice, dissolved in water, and precipiated in glass vessels with a slight excess of hydrochloric acid. The hloride was washed several times with cold water and then crystalized from aqueous solution eight times, the last five crystallizations being arried out wholly in platinum, with centrifugal drainage after each crysallization. In crystallizing the lead chloride the whole sample was ot dissolved at one time, but the same mother liquor was used for disolving several portions of the original salt. Needless to say, the chloide was not exposed to contact with the products of combustion of lluminating gas, lest lead sulphate be formed.

Sample B was prepared from commercial lead nitrate. This salt was lissolved and crystallized from dilute nitric acid once in glass and six

[1] Richards and Wells, Pub. Car. Inst., No. 28, 19 (1905).

[2] Abrahall, J. Chem. Soc. Proc., 1892, p. 660.

[3] Baxter, Proc. Am. Acad., 39, 249 (1903).

times in platinum vessels, with centrifugal drainage. Hydrochloric acid was then distilled into a large quartz dish, and the solution of the nitrate was slowly added with constant stirring with a quartz rod. The chloride was freed from aqua regia as far as possible by washing with cold water, and was once crystallized from aqueous solution in quartz dishes to remove last traces of aqua regia. Finally the salt was crystallized three times in platinum.

It could reasonably be expected that both of these samples were of a high degree of purity; nevertheless, upon heating the salt in an atmosphere of hydrochloric acid, the salt itself turned somewhat dark, and upon solution of the fused salt in water a slight dark residue remained. Although in a few preliminary experiments attempts were made to determine this residue by filtration and ignition, it was subsequently found that even a small filter paper adsorbs appreciable amounts of lead compounds from a solution of the chloride, which cannot be removed by washing with water. From three to thirteen hundredths of a milligram of residue were obtained in several blank experiments, by ignition of filters through which half per cent. solutions of lead chloride had been passed, with subsequent, very thorough washing. In order to avoid the uncertainty of this correction, further attempts were made to obtain a sample of the salt which would give a perfectly clear solution in water after fusion, and thus render filtration unnecessary. With this end in view a considerable quantity of Sample A was fused in a large platinum boat in a current of hydrochloric acid. The fused salt was powdered in an agate mortar, dissolved in water in a platinum vessel, and the solution was freed from the residue by filtration through a tiny filter in a platinum funnel into a platiunm dish, where it was allowed to crystallize. This sample was then twice recrystallized with centrifugal drainage. Notwithstanding the drastic treatment to which it had been subjected, when a portion of this material was fused in hydrochloric acid, the same darkening as before was observed, and the same residue was obtained. The suspicion that the difficulty was due to dissolving of the filter paper by the solution of the salt[1] led to a second more successful attempt by crystallization from hydrochloric acid solution in platinum vessels. In this way it was found possible to prepare salt which showed no tendency to darken upon heating, and which, after fusion, left absolutely no residue upon solution in water. Portions of Samples A and B were thus recrystallized three times more. Since these two specimens of material gave identical results, for two final experiments portions from each of these samples were mixed and then subjected to three additional crystallizations. This last sample was designated Sample C.

[1] Mr. P. B. Goode in this laboratory has recently found a similar difficulty with the chlorides of the alkaline earths.

Method of Analysis.

he lead chloride contained in a weighed platinum boat was first fused current of pure, dry hydrochloric acid gas. This gas was generated dropping concentrated sulphuric acid into concentrated hydrochloric ., and after being washed with a saturated solution of hydrochloric , was passed through five towers filled with beads moistened with hly boiled, concentrated sulphuric acid, to dry the gas. It has al- ly been shown that phosphorus pentoxide may not be used for this ɔose.[1] After the salt had cooled, the hydrochloric acid was displaced dry nitrogen, and this in turn by dry air. Nitrogen was prepared ɔassing air charged with ammonia over red-hot rolls of copper gauze, excess of ammonia being removed by means of dilute sulphuric acid. gas was passed over beads moistened with a dilute silver nitrate tion and over solid caustic potash to remove sulphur compounds carbon dioxide respectively, and was finally dried by concentrated huric acid and phosphorus pentoxide. The air was purified and d in a similar fashion. The apparatus for generating the hydro- ɪric acid and for purifying the hydrochloric acid and nitrogen was ɜtructed wholly of glass with ground-glass joints. The platinum t containing the fused chloride was next transferred to a weighing .le without exposure to moist air, by means of the bottling apparatus, ɔh has frequently served for a similar purpose in many atomic weight ɜstigations in this laboratory.[2] After standing some time in a desic- ɪr in the balance room, the weighing bottle was weighed. In most he analyses the lead chloride was dissolved from the boat by pro- ɡed contact with boiling water in a Jena glass flask. In the last two ,yses, in order to show that no error was introduced through solu- y of the glass, the solution was prepared in a large platinum retort, was not transferred to the precipitating flask until cold.

ery nearly the necessary an ount of pure silver was then weighed and dissolved in a redistilled nitric acid diluted with an equal volume vater in a flask provided with a column of bulbs to prevent loss by tering. After the silver was all dissolved, an equal volume of water added, and the nitrous fumes were expelled by gentle heating. The tion was then further diluted until not stronger than one per cent., added slowly, with constant agitation, to the solution of lead chlo- contained in the precipitating flask. The precipitation and hand- of the silver chloride were conducted in a room lighted with ruby t. The flask was shaken for some time and allowed to stand for a days, with occasional agitation, until the supernatant liquid had ɔme clear. Thirty cubic centimeter portions of the solution were

[1] Baxter and Hines, This Journal, 28, 779 (1906).

[2] Richards and Parker, Proc. Am. Acad. Arts and Science, 32, 59 (1896).

then removed and tested with hundredth normal silver nitrate and sodium chloride, in a nephelometer,[1] for excess of either chloride or silver, and, if necessary, standard silver nitrate or sodium chloride was added, and the process of shaking and testing repeated until the amounts of silver and chloride were equivalent. The test solutions were always returned to the flask, since they contained appreciable amounts of silver chloride, and the weight of silver chloride subsequently obtained was corrected for the quantity thus introduced. Furthermore, if an excess of silver was found, a negative correction of an equivalent quantity of silver chloride was necessary.

After the exact end point had been obtained, about two tenths of a gram of silver nitrate in excess was added in order to precipitate the dissolved silver chloride, and the flask was thoroughly shaken, and allowed to stand again until the solution was perfectly clear. The silver chloride was washed, first several times with a very dilute silver nitrate solution containing four hundredths of a gram per liter, and then eight times with pure water. It was next transferred to a Gooch crucible and dried for several hours in an electric oven, the temperature being gradually raised to 180°, and was cooled in a desiccator and weighed. In every case the moisture retained by the precipitate was determined by fusion in a small porcelain crucible. The silver chloride, dissolved in the filtrate and washings, was determined by comparison with standard solutions in the nephelometer in the usual manner. Care was taken to treat both tubes in exactly the same manner, and final readings were taken only when the ratio had become constant. Before proceeding to the nephelometer tests, however, the filtrate and washings were passed through a very small filter in order to collect a small quantity of asbestos shreds mechanically detached from the Gooch crucible. The filter was ignited and weighed, the ash being treated with a drop of nitric and hydrochloric acids in order to convert any reduced silver into chloride. In order to find out whether lead or silver nitrates were appreciably adsorbed by the filter paper, a solution containing lead nitrate, silver nitrate, and nitric acid of the concentration of these filtrates, was passed through several small filter papers, which were then very carefully washed. In four cases, after incineration of the papers, there was found, —0.00001, +0.00002, +0.00003, +0.00001 gram of residue, exclusive of ash. This correction is so small that it is neglected in the calculations. In all the analyses the platinum boat behaved admirably, the loss in weight never amounting to more than a few hundredths of a milligram.

The balance used was a short arm Troemner, easily sensitive to a fiftieth of a milligram. The gold-plated brass weights were carefully standardized to hundredths of a milligram. All the weighings were

[1] Richards and Wells, Am. Chem. J., 31, 235 (1904); 35, 510 (1906).

y substitution with tare vessels as nearly like those to be weighed ible.

um corrections: The values of the density of lead chloride as y various observers range from 5.78 to 5.805,[1] the mean of the ccurate determinations being 5.80. This gives rise to a vacuum on of +0.000062 for each apparent gram of lead chloride, the of the weights being assumed to be 8.3. The other vacuum ons applied were silver chloride +0.000071, and silver —0.000031. nalyses which were carried to a successful completion are recorded ables.

THE ATOMIC WEIGHT OF LEAD.

Series I. $PbCl_2$: 2Ag.

mple of $PbCl_2$.	Weight of $PbCl_2$ in vacuum. Grams.	Weight of Ag in vacuum. Grams.	Weight of Ag added or subtracted. Gram.	Corrected weight of Ag. Grams.	Atomic weight of Pb. Ag=107.930. Cl=35.473.	Atomic weight of Pb. Ag=107.880. Cl=35.457.
A	4.67691	3.63061	—0.00074	3.62987	207.179	207.079
A	3.67705	2.85375	0 00000	2.85375	207.189	207.089
A	4.14110	3.21388	+0.00020	3.21408	207.173	207.073
A	4.56988	3.54672	0.00000	3.54672	207.185	207.085
B	5.12287	3.97596	—0.00028	3.97568	207 201	207.101
B	3.85844	2.99456	0.00000	2.99456	207.186	207.086
B	4.67244	3.62628	0.00000	3.62628	207.189	207.089
C	3 10317	2.40837	0.00000	2.40837	207.188	207.088
C	4.29613	3.33427	—0.00020	3.33407	207.202	207.102
.....					207.188	207.088

Series II. $PbCl_2$: 2AgCl.

mple of $PbCl_2$.	Weight of $PbCl_2$ in vacuum. Grams.	Weight of AgCl in vacuum. Grams.	Loss on fusion. Gram	Weight of asbestos. Gram.	Weight AgCl from wash waters. Gram.	Corrected weight of AgCl. Grams.	Atomic weight of Pb. Ag=107.930. Cl=35.473	Atomic weight of Pb. Ag=107.880. Cl=35.457
A	4.67691	4.82148	0.00100	0 00021	0.00204	4.82273	207 188	207.088
A	4.14110	4.26848	0.00020	0 00008	0.00180	4.27016	207.192	207.092
B	5.12287	5.28116	0.00054	0 00013	0.00197	5.28272	207.181	207.081
B	3.85844	3.97759	0.00035	0.00033	0.00192	3.97949	207 136	207.036
C	3.10317	3 19751	0.00045	0.00014	0.00189	3.19909	207.261	207.161
C	4.29613	4.42730	0.00020	0.00004	0.00268	4.42982	207.204	207.104
.....							207.193	207.093
rejecting the least satisfactory analyses, 13 and 14.....							207.191	207.091
of Series I and II.....							207.190	207.090

close agreement of the averages of the two series is strong evi- hat no constant error, such as occlusion, affects the results. more, in all, 19.55663 grams of silver produced 25.98401 grams chloride, whence the ratio of silver to silver chloride is 132.865, in close agreement with the result 132.867 obtained by Richards

[1] dolt-Börnstein-Meyerhoffer, Tabellen.

and Wells.[1] The different samples, A, B, and C, all give essentially identical results.

It appears, then, that if the atomic weight of silver is taken as 107.93 (O=16.000), the atomic weight of lead is 207.19, nearly three tenths of a unit higher than the value now in use. If the atomic weight of silver is 107.88, a value probably nearer the truth than 107.93, lead becomes 207.09, a number still much higher than that depending upon Stas's syntheses, as is to be expected.

We are greatly indebted to the Carnegie Institution of Washington for assistance in pursuing this investigation, also to Dr. Wolcott Gibbs and to the Cyrus M. Warren Fund for Research in Harvard University for many indispensable platinum vessels.

CAMBRIDGE, MASS.,
October 18, 1907.

CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE UNDER HIGH PRESSURES OF OXYGEN.[2]

BY E. B. SPEAR.

Received October 12, 1907.

Introduction.

The mechanism of catalysis by means of the metals in their different forms and especially their decomposing effect on hydrogen peroxide has been the subject of a great deal of very thorough experimental investigation. Since Bredig published his work on the preparation of colloidal solutions by electrical[3] means, the study of catalysis has had an additional impetus, and our knowledge of the subject has been greatly increased by the investigations of this author and his co-workers, Müller v. Berneck,[4] K. Ikeda,[5] W. Reinders,[6] Fortner,[7] Teletow[8] and v. Antropoff.[9]

It has been conjectured by several authors that the *dissolved* or *chemically* bound oxygen in the metal phase plays a necessary part in the catalytic decomposition of hydrogen peroxide. The experiments of Haber and S. Grinberg,[10] Euler,[11] and of Engler and Wöhler[12] indicate

[1] *Loc. cit.*
[2] Dissertation, Heidelberg (1907).
[3] Z. angew. Chem., 1898, p. 951.
[4] Z. physik. Chem., 31, 258.
[5] *Ibid.*, 37, 2.
[6] *Ibid.*, 37, 323.
[7] Ber., 37, 798.
[8] Z. Elektrochemie, 12, 581.
[9] *Ibid.*
[10] Z. anorg. Chem., 18, 37.
[11] Oefers af. K Vetenskaps Förhandl., 1900, p. 267.
[12] Z. anorg. Chem., 29, 1.

that the presence of oxygen is necessary before many of these catalytic processes take place.

Bredig and Müller v. Berneck[1] attempted to investigate the influence of the dissolved or chemically bound oxygen on the catalytic decomposition of hydrogen peroxide by subjecting their colloidal solutions to reduced pressure before using them as catalyzers. They were not able, however, to discover any marked difference in either the rate of reaction or in the reaction constant as a result of this treatment. Bredig,[1] therefore, concluded that the decrease in catalytic effect observed by Gernez, after he had boiled his colloidal solutions, or had heated his platinum black, was caused by some change that the *metal* had undergone, rather than by the loss of oxygen. This assumption of Bredig's agrees very well with the experimental facts, at least in the case of colloidal solutions, because of the coagulating effect of the boiling. Again, if the loss of oxygen were the only cause of the observed retardation in the rate, the colloid must very quickly regain its original activity because oxygen is a product of the decomposition of hydrogen peroxide. It is doubtful if this is the case.[2] It might be pointed out, however, that if a *compound* of platinum and oxygen is an essential factor in the catalysis it does not necessarily follow that this compound will be destroyed by pumping out the *dissolved* oxygen unless it has an appreciable dissociation pressure and a rapid rate of decomposition. Bredig's experiments are not conclusive, they indicate that the *dissolved* oxygen does not play a vital part in the reaction. This latter statement is in accordance with the results given in this article.

Liebermann and Genersich[2] endeavored to investigate the rôle of the oxygen in the decomposition of peroxide by boiling their colloidal solutions or by bubbling gas through them in order to free them from oxygen. They then treated different portions of the catalyzer thus prepared with oxygen, hydrogen and nitrogen gas respectively and compared the effectiveness of each portion with that of the original colloidal solution. Unfortunately we are not able to conclude very much from their experiments because they worked with much too concentrated solutions (about 3 per cent. hydrogen peroxide). Their reaction mixture must have been saturated with oxygen as a product of the catalysis itself before they could make a single titration to learn the progress of the reaction. Their gasometric method also does not give us the necessary information, for the difference in height of the two columns of mercury is not an accurate measure of the amount of decomposition during the first few moments of the reaction because of supersaturation. But it is precisely this amount that we wish to know.

[1] *Loc. cit.*, p. 336.

[2] Liebermann and Genersich (Arbeiten aus den hy. Institut der Universität Budapest; Archiv. ges. Physiol., 104, 139) state that their platinum solutions regained their original activity in a few instances.

The object of the work described here was to ascertain experimentally the effect of increasing the concentration of oxygen on the catalytic decomposition of hydrogen peroxide. This was accomplished by means of the apparatus described on page 198.

Experimental.

Preparation of the Solutions.—The colloidal solutions used in this work were prepared by Bredig's well-known electrical method. The pure metals were obtained from Heraeus, Hanau. The colloidation of platinum took place in neutral, that of all the other metals mentioned in dilute M/1000 alkaline solutions as free as possible from carbonate. The concentrations of the platinum, palladium, iridium and gold solutions were determined by precipitating the metals with hydrogen sulphide in dilute sulphuric acid solution, heating the sulphides to constant weight and weighing as pure metal. The colloidal silver solutions were analyzed by dissolving the metal in concentrated nitric acid, evaporating almost to dryness, diluting and titrating with a potassium sulphocyanate solution according to the method of Volhard. The hydrogen peroxide solutions were prepared by diluting a 30 per cent. preparation from Merck with pure water.

The water used in the preparation of the solutions was purified by Hulett's method.[1] The conductivity of the water thus prepared was not determined because these measurements are not sufficiently delicate to be regarded as a safe criterion for the absence of many of the so-called *poisons* for colloidal platinum; furthermore, many of these poisons are non-electrolytes.

Cleansing of the Glass Apparatus.—Experience teaches that reproducable results cannot be obtained with metal catalysis unless the glass with which the solutions come in contact has been cleaned with extreme care. New vessels should be boiled for some time with concentrated hydrochloric acid and then with pure water. Vessels not in use should be carefully cleaned and placed in pure water. Immediately before they are required they should be well steamed out, using pure water to generate the steam.

In spite of the most careful manipulation, however, one often obtains irregular results that cannot be repeated. This is especially the case where the experimental difficulties preclude the possibility of preventing occasional poisoning effects. If many irregular results were obtained with a particular set of solutions they were thrown out, the glassware thoroughly cleaned and new solutions made up.

Description of the Bomb.—The experiments under pressure were carried out in a bomb made of "Rotguss" (see Fig. 1, *a*, p. 198). The ring *c* was for screwing the lid *b* on to body of the bomb *a*. The manipulation is much

[1] Z. physik. Chem., 21, 297.

more difficult when the ring *c* and the lid *b* consist of one piece as in the case of bomb *b* Fig. 3, p. 204. The compressed gas was conducted into the bomb through the metal tube *e*. The detachable tube *f* was connected with the glass tube *g* by a piece of rubber tubing *p*. The glass tube *g* dipped into the reaction mixture contained in the glass vessel *d* and served as a siphon through which small portions of the liquid in *d* could be taken out at will and analyzed. The short metal tubes *t* and *q* were soldered on to the lid. The bomb was made gas-tight by means of a steel ring, *m*, and two rings of soft lead, *l*, which were each about 2 mm. thick. This arrangement is not entirely satisfactory and difficulty was experienced in keeping the bomb from leaking at high pressures. The original plan of the author seems much preferable, but owing to a misunderstanding it was not carried out by the firm that made the bomb (see Fig. 1, *b*). Here there is only *one* lead ring employed and no plain surface between the body of the bomb and the lid. The under side of the thread *w* on the bomb and the upper side of the thread on the ring *c* should be right-angled and not beveled as it is in the figure.

Fig. 1(*a*).

The bomb was placed in a thermostat and partially filled with water in order that the reaction mixture might rapidly come to and remain

Fig. 2(b).

at the temperature of the thermostat. The tube *e* was connected with a manometer by means of a bent metal tube *z*, Fig. 3, p. 204 and the manometer was in turn connected with an ordinary oxygen bomb. By means of this arrangement a pressure of 1–100 atmospheres of oxygen gas could be obtained at will in the reaction-bomb. It was found possible to open the valve *i* so slowly that the liquid ran out of *f* drop by drop or in a gentle stream. At very high pressures (100–250 atmospheres) the liquid came out as a spray, owing to the expansion of the dissolved gas.

Blank experiments without a catalyzer proved that a small portion of the hydrogen peroxide was decomposed on being forced out through the metallic tube *f*. This difficulty was overcome by coating the inside of the tube with paraffin which was accomplished by filling the tube with a saturated alcoholic solution of paraffin and then sucking air through. It was found necessary to renew the coating every two or three days. These precautions prevented the decomposition of the hydrogen peroxide even when the solution was allowed to stand some time in the tube.

Analytical Method.—The progress of the reaction was followed by the method so often employed by Bredig and his co-workers, *viz.*, by titrating the still undecomposed hydrogen peroxide in a known volume with a dilute solution of potassium permanganate (0.24 gram per liter) after the addition of a few cubic centimeters of dilute sulphuric acid. Occa-

sionally it was found necessary to add a drop of manganous sulphate to start the reaction.

Operation under Pressure (1–100 Atmospheres).—The colloidal solutions were diluted to the desired concentration and kept at 25° for at least twelve hours before the experiment because very irregular results are obtained, if freshly diluted solutions are employed for catalytic purposes. The hydrogen peroxide solutions were also warmed to 25° before the mixing took place.

The desired amounts of the different solutions were now placed in the reaction vessel and thoroughly mixed by stirring with a glass rod. Two cc. were immediately pipetted out and titrated. In many cases, however, the first titration was made after the pressure had been applied. The lid was then placed on the bomb and quickly screwed down. The bomb was connected with the source of pressure as quickly as possible and the pressure slowly applied. In about ten minutes after the first titration the valve *i* was slowly opened and 5 to 10 cc. of the liquid were allowed to run out before the second sample for analysis was collected in order that no liquid that had remained in the tube *f* might be titrated and possibly cause an error in the result. The sample thus obtained was violently shaken to free the liquid from gas before the usual 2 cc. were measured for titration.

The compressed oxygen used was that generally employed for analytical purposes. In order to ascertain if it contained anything poisonous to colloidal platinum, the gas was bubbled through a hydrogen peroxide solution for one-half hour. No difference in the rate could be detected resulting from this treatment. One dare not bubble gas through the colloidal solutions.[1] In later experiments the possibility of poisoning by the compressed oxygen was reduced very greatly by the use of the glass vessel described on p. 202.

In order to compare the results obtained under pressure with those under ordinary circumstances, experiments with the same solutions in the same vessel on the same day were carried out in the bomb at atmospheric pressure. The solutions were mixed as already described and the first titration made as usual. The glass vessel containing the reaction mixture was then placed in the bomb and the lid screwed on. In about ten minutes a pressure of 1–3 atmospheres was applied and a sample run out as before. The pressure in the bomb was then relieved.

Catalysis with Colloidal Platinum.—In the course of this investigation irregular results were occasionally obtained and the reactions were considered poisoned or accelerated if they could not be repeated under the same experimental conditions. More than 200 measurements were made with colloidal platinum, a few of which are given below.

[1] Liebermann and Generisch, *Loc. cit.*

In this article:

t = time in minutes;

Titer = number of cubic centimeters of the potassium permanganate solution used to titrate the undecomposed hydrogen peroxide.

P = pressure in atmospheres;

Conc. = concentration;

Atm. = atmospheres;

Exp. = experiment;

k = reaction constant calculated from the integrated formula,

$$k = \frac{1}{t_2 - t_1} \ln \frac{A - x_1}{A - x_2},$$

where A is the titer at the beginning of the reaction, x_1 and x_2 the amount of hydrogen peroxide decomposed at the time t_1, t_2 expressed in cubic centimeters of potassium permanganate solution. In every case, k has been calculated from pairs of consecutive measurements. The concentration of the metal in the reaction mixture is expressed in gram atoms, that of the hydrogen peroxide in gram mols. per liter.

TABLE 1.

Concentrations.	Expt. 63(a). P = 70. t.	0.4342 k.	Expt 63(b). P = 1. t.	0.4343 k.	Concentrations.	Expt. 121. P = 70. t.	0.4343 k.	Expt. 122. P = 1. t.	0.4343 k.
	30.5	0.0028	29	0.0023					
$Pt = \frac{1}{145,000}$	62.5	0.0029	60.5	0.0024	$Pt = \frac{1}{100,000}$	10	0.0176	10	0.0150
$H_2O_2 = \frac{1}{30}$	76.5	0.0029	76	0.0024	$H_2O_2 = \frac{1}{30}$	20	0.0169	21	0.0186
						30	0.0187	35	0.0174
Duplicates of	Expt. 64. P = 70.		Expt. 65. P = 1.			Expt. 125. P = 70.		Expt. 126. P = 1.	
63 (a) & (b)	39	0.0024	29	0.0021	$Pt = \frac{1}{2,000,000}$	80	0.00028	29	0.00047
	77	0.0027	67	0.0025		236	0.00023	71	0.00028
	109.5	0.0027	111.5	0.0027	$H_2O_2 = \frac{1}{30}$	382	0.00020	..	..
	Expt. 80. P = 70.		Expt 81. P = 1.		Duplicate of			Expt. 127. P = 1.	
$Pt = \frac{1}{150,000}$	29	0.0040	29	0.0037	126			118	0.00022
$H_2O_2 = \frac{1}{30}$	74.5	0.0059	63	0.0047				359	0.00011
	126.5	0.0042	106.5	0.0052					
	167	0.0051							
	Expt. 119. P = 70.		Expt. 120. P = 1.						
$Pt = \frac{1}{200,000}$	14.5	0.0069	18	0.0057					
$H_2O_2 = \frac{1}{30}$	34.5	0.0067	40	0.0061					
	56.5	0.0070	63	0.0065					
	78.5	0.0069	90	0.0063					

lthough a gas does not dissolve very rapidly in a motionless liquid nay safely assume that the concentration of the oxygen in the mixture very much greater towards the end of the reaction in the experiments er high pressure than in those at a pressure of one atmosphere, yet constants in the two cases are almost identical. Quantitative ex- ments with regard to the amount of dissolved oxygen will be given .

ne objection might be raised to the foregoing results that the com- sed oxygen contained a poison or an accelerator for the reaction se influence exactly counterbalanced the effect of the increased con- ration of the oxygen. This possibility was very much reduced by use of the glass vessel described below. By this arrangement the ace of contact between the gas and the reaction mixture was reduced ery small dimensions, so that not very much of the outer gas could nto the reaction mixture during the experiment, while the chemically oxygen that had been generated by the catalysis could get out of liquid only under high pressure. By beginning with the correspond- concentration of hydrogen peroxide in the reaction mixture it was possible to obtain any desired concentration of oxygen, while the outer compressed gas served to keep the generated oxygen from escaping from the liquid.

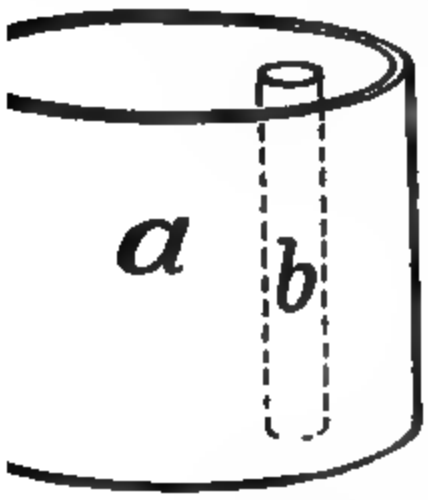


Fig. 2.

a (Fig. 2) is a glass vessel (ca. 3 cm. deep) that exactly fitted into the vessel in which the reaction was carried out. The siphon tube *g* (Fig. 1) fitted just as neatly into tube *b* (Fig. 2). Vessel *a* was placed on the surface of the reaction mixture and was free to sink as the liquid was siphoned out for analysis. If the glass was free from grease liquid rose between the sides of the inner and outer vessels to the er edge of vessel *a*. A series of results obtained by this method is n in Table 2.

TABLE 2.

	Expt. 250. P = 1.		Expt. 251. P = 60.			Expt. 252. P = 1.		Expt. 253. P = 70.	
ntrations.	*t.*	0.4343 *k.*	*t.*	0.4343 *k.*	Concentrations.	*t.*	0.4343 *k.*	*t.*	0.4343 *k.*
$\frac{1}{200,000}$*	10	0.0072	10	0.0072	$Pt = \frac{1}{200,000}$	10	0.0055	10	0.0038
$= \frac{1}{25}$	30	0 0087	30	0.0072	$H_2O_2 = \frac{1}{2}$	30	0.0060	30	0.0037
	60	0.0091	60	0.0081		60	0.0064	[illegible]	0.0041
	92	0.0094	90	0.0076		127	0.0061	..	...

* Preparation several months old.

Duplicates of	Expt. 256. P = 1.		Expt. 257. P = 70.		Duplicates of	Expt. 254. P = 1.		Expt. 255. P = 70.	
254 & 255	11	0.0050	10	0.0055	252 & 253	10	0.0059	12	0.0054
	30.5	0.0065	30	0.0066		30	0.0074	30	0.0060
	60	0.0070	60	0.0080		60	0.0074	60	0.0073
	117	0.0064	139	0.0094		120	0.0078	177	0.0089
	188	0.0053	169	0.0122					

If all the oxygen generated in Expts. 255 and 257 remained in solution the pressure toward the end of the reaction must have been 120 atmospheres. We may, therefore, safely assume that the partial pressure of the free oxygen in solution was 30 to 40 times as great as in the corresponding experiments, 254 and 256, yet we see that the rate was practically the same in both cases.

The influence of still greater oxygen concentrations (100 to 200 atmospheres) was investigated by the aid of the apparatus shown in Fig. 3. As the author could not obtain the use of a pump suitable for the purpose, the high pressure was obtained by allowing liquid oxygen to evaporate. *a* is the reaction bomb already described. It was placed as usual in a thermostat and was connected with a manometer for high pressures (1–1000 atmospheres). The manometer was in turn connected with the bomb *b*. If now a calculated amount of liquid oxygen was put into bomb *b* and allowed to evaporate, the corresponding pressure was obtained in the reaction bomb *a*.

It was impossible to pour liquid oxygen into the bomb without cooling it before hand if the liquid came into contact with the metal, because the heat capacity of the latter is so great that the liquid evaporated in a very few minutes. Cooling the bomb before introducing the oxygen was too expensive and impracticable. This difficulty was overcome by pasting strips of asbestos paper on the inner walls of the bomb and blowing a glass bulb inside it. The narrow space between the glass and the metal was filled with zinc oxide. With this arrangement the liquid oxygen (ca. 400 cc.) evaporated completely within thirty minutes, consequently, the high pressure was obtained quickly enough for the purposes of the experiment.

Details of the Experiments at High Pressure.—The experiment was begun in the usual manner and a pressure of 70–80 atmospheres was obtained in the reaction bomb from the usual source. The liquid oxygen was next poured into the bomb *b*, and the whole apparatus connected as in the figure. As soon as the pressure in the bomb, *b*, had risen to 70–80 atmospheres, bomb *a* was connected with the source of pressure by opening valve *d* (Fig. 3). The pressure rose to its maximum in about thirty minutes but occasionally fell somewhat towards the end of the experiment because the apparatus was not always gas-tight.

An analysis of the gas obtained from the liquid oxygen gave a content

of 93.5 per cent. of oxygen. The remainder consisted principally of nitrogen. The results are given in Table 3.

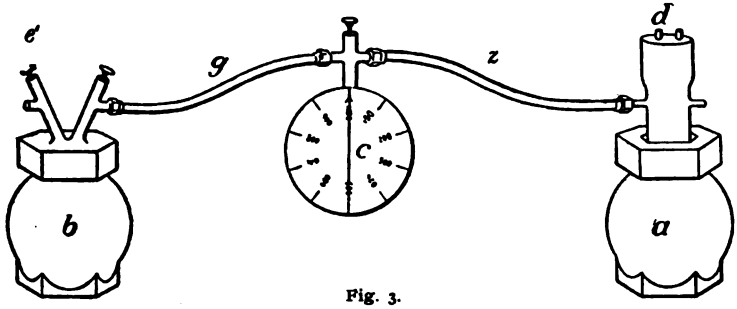


Fig. 3.

In Experiments 259 and 267 an open glass vessel was used in bomb *a*, while in Experiment 268 the vessel described on p. 202 was used. We see quite clearly from these results that a high concentration of oxygen has no perceptible effect on the catalysis.

TABLE 3.

	Expt. 259. P = 160 → 140.		Expt. 263. P = 70.			Expt. 266. P = 1.		Expt. 267. P = 200 → 100.	
Concentrations.	*t.*	0.4343 *k.*	*t.*	0.4343 *k.*	Concentrations.	*t.*	0.4343 *k.*	*t.*	0.4343 *k.*
$Pt = \frac{1}{200,000}$	10.5	0.0042	9	0.0026	$Pt = \frac{1}{350,000}$	10	0.0020	12.5	0.0020
$H_2O_2 = \frac{1}{2}$	32	0.0050	30	0.0047	$H_2O_2 = \frac{2}{3}$	30.5	0.0026	32	0.0028
	63.5	0.0049	60	0.0050		67	0.0029	62	0.0030
	107	0.0052	120.5	0.0047		151.5	0.0025	99	0.0026
	193	0.0050	197.5	0.0049		346.5	0.0021	174	0.0023
	256	0.0052	...	..				269	0.0019

	Expt. 268. P = 200 → 160.		Expt. 269. P = 1.	
$Pt = \frac{1}{350,000}$	10	0.0025	10	0.0033
$H_2O_2 = \frac{1}{3}$	26.5	0.0024	30	0.0036
	60	0.0030	60	0.0032
	120	0.0022	120	0.0022
	231	0.0019	..	..

The effect of increasing the concentration of the oxygen was tried where the *k* decreased from the beginning of the reaction. In such cases it is generally assumed that some one of the solutions contains a poison for the catalysis. Experiments 270 and 271 were carried out with the same solutions 8 days later than 260–3.

TABLE 4.

	Expt. 260. P = 1.		Expt. 261. P = 70.			Expt. 262. P = 1.		Expt. 263. P = 70.	
Concentrations.	*t.*	0.4343 *k.*	*t.*	0.4343 *k.*	Concentrations.	*t.*	0.4343 *k.*	*t.*	0.4343 *k.*
$Pt = \frac{1}{200,000}$	10	0.0075	10	0.0069	Duplicates	10	0.0047	9	0.0026
$H_2O_2 = \frac{1}{20}$	30	0.0068	29	0.0060	of 260 & 261	32.5	0.0037	30	0.0047
	60	0.0055	60	0.0057		121.5	0.0036	60	0.0050
	120	0.0050	117.5	0.0052		207.5	0.0024	120.5	0.0047
								197.5	0.0049

	Expt. 270. P = 1.		Expt 271. P = 70.	
$Pt = \frac{1}{200,000}$	10	0.0043	9	0.0044
$H_2O_2 = \frac{1}{2}$	31	0.0042	30	0.0040
	59	0.0043	61	0.0042
	137	0.0035	126	0.0038
	215	0.0032	..	..

Many authors have thought that the platinum becomes more active through the presence of the hydrogen peroxide or of the oxygen. A glance at the tables given above will reveal the fact that the k often increases in value until the very end,[1] while in many experiments (usually with different colloidal solutions) k goes through a maximum.[2] A large number of experiments not given here were carried out and in every case no relation was found between the amount of dissolved oxygen and the rate of reaction, or the course of k.

Experiments with Colloidal Gold under Pressure.—The gold catalysis of hydrogen peroxide at ordinary pressure has been studied by Bredig and Reinders.[3] Experiments under high pressures of oxygen gave similar results to those obtained with platinum.

The reaction mixture was made alkaline because the rate in neutral or dilute acid solutions is very slow. The alkaline solution was made according to Paul's method by dissolving freshly cut sodium in water that had been boiled to free it from carbon dioxide.

TABLE 5.

Concentrations.	Exp. 155. P = 1. t.	0.4343 k.	Exp. 157. P = 80 t.	0 4343 k.	Concentrations.	Exp. 168. P = 1. t.	0.4343 k.	Exp. 169. P = 80. t.	0.4343 k.
$Au = \frac{1}{200,000}$	22.5	0.0017	20	0.0027	$Au = \frac{1}{200,000}$	20	0.0045	20	0.0040
$NaOH = \frac{M}{55}$	40	0.0025	40	0.0027	$NaOH = \frac{2M}{55}$	40	0.0045	40	0.0051
$H_2O_2 = \frac{1}{30}$	70	0.0033	70	0.0026	$H_2O_2 = \frac{1}{30}$	60	0.0079	60	0.0056
	100.5	0.0046	95	0.0044		80	0.0045	..	..
	$96.7 = t_{A/2}$		$100 = t_{A/2}$			$52.3 = t_{A/2}$		$55.6 = t_{A/2}$	
$Au = \frac{1}{400,000}$	Expt. 154. P = 1.		Expt. 160. P = 80.		$Au = \frac{1}{400,000}$ [4]	Expt. 162. P = 1.		Expt. 163. P = 1.	
$NaOH = \frac{1}{55}$	19.5	0.0020	20	0.0017	$NaOH = \frac{2M}{55}$	20	0.0021	21	0.0019
$H_2O_2 = \frac{1}{30}$	70	0.0027	50	0.0024	$H_2O_2 = \frac{1}{30}$	40	0.0011	60	0.0011
						60	0.0011		
					Duplicates	Expt. 164. P = 60.		Expt. 163. P = 80.	
					of 162 & 3	20	0.0018	21	0.0019
					under pres.	40	0.0012	60	0.0015
						60	0.0016	81	0.0013
						80	0.0013	..	...

[1] See Experiments 65, 80, 81, 121, 250, 253, 254, 255, 257, 244, 245.

[2] See Experiments 232, 237, 266, 267, 268, 269.

[3] *Loc. cit.*

[4] Partly coagulated.

Experiments with colloidal gold more dilute with respect to alkali han $\frac{M}{100}$ gave very irregular results, very probably because of the presence of a varying amount of carbon dioxide. It is very difficult under complicated experimental conditions to prevent errors from this source.

As Bredig and K. Ikeda have pointed out, the metal catalysis of hydrogen peroxide in alkaline solutions does not follow the simple law for first-order reactions. Nevertheless, the values of k given in the table above have been calculated according to this law because they serve as a method of comparison if the same intervals of time are considered. Wherever it was practicable the time $t_{A/2}$ necessary to decompose one-half the hydrogen peroxide has been calculated by interpolation.

Experiments with Colloidal Palladium under Pressure.—The decomposition of hydrogen peroxide by colloidal palladium under ordinary pressure has been studied by Bredig and Fortner. The reaction under high pressures of oxygen has been followed by the author in precisely the same manner as in the case of gold. The results are very regular and show that the palladium solutions used were very much more active than those of the other metals having the same concentration.

TABLE 6.

	Expt. 175. P = 1.		Expt. 176. P = 80			Expt. 177. P = 1.		Expt. 178 P = 70.	
Concentrations.	t.	0.4343 k.	t.	0.4343 k.	Concentrations.	t.	0.4343 k.	t.	0.4343 k.
Pd = $\frac{1}{1,200,000}$	20	0.0073	20	0.0069	Duplicates of	20	0.0067	20	0.0082
H_2O_2 = $\frac{1}{30}$	40	0.0088	43	0.0092	175 & 176	40	0.0104	40	0.0107
NaOH = $\frac{1}{55}$	60	0.0093	60	0.0093		60	0.0110	60	0.0134
	38 = $t_{A/2}$		38.7 = $t_{A/2}$			36.1 = $t_{A/2}$		34.4 = $t_{A/2}$	
	Expt. 179. P = 1.		Expt. 180. P = 80.						
Duplicates	20	0.0070	20	0.0072					
of 175 & 6	40	0.0095	43.5	0.0092					
			60	0.0100					
	37.4 = $t_{A/2}$		38.1 = $t_{A/2}$						

Investigation with Colloidal Iridium.—The catalytic properties of colloidal iridium have not yet been carefully worked out.[1] It has been the object of the following experiments to go into the question only in so far as it was necessary in order to ascertain the effect of high concentrations of oxygen on the catalytic decomposition of hydrogen peroxide by colloidal iridium.

The electrical colloidation of iridium is much more difficult than that of the other metals used in these experiments. Iridium is brittle and the wires often fuse together because of the large amount of current required (14–16 amperes, 70 volts).

[1] Experiments on this problem are being carried out by Dr. Brossa, in Heidelberg.

No experiments were carried out with iridium in acid or neutral solution. Those in dilute alkaline solution show the remarkable fact that the reaction very nearly follows the law for first-order reactions. No very great weight should be laid on this result until the subject has been thoroughly investigated, because all the following experiments with colloidal iridium were carried out with a single preparation.

TABLE 7.

Concentrations.	Expt. 182. P = 1. t.	0.4343 k.	Expt. 183. P = 70. t.	0.4343 k.	Concentrations	Expt. 184. P = 70. t.	0.4343 k.	Expt. 185. P = 1. t.	0.4343 k.
$Ir = \frac{1}{60,000}$ [1]	20	0.0054	20	0.0048	Duplicates	21	0.0062	21	0.0049
$NaOH = \frac{1}{55}$	40	..	40	0.0052	of 183 & 182	60	0.0049	40	0 0052
$H_2O_2 = \frac{1}{30}$	60	0.0060	60	0.0058				60	0.0051
						$56.3 = t_{A/2}$		$60 = t_{A/2}$	

Duplicates	Expt. 186. P = 70. t.	0.4343 k.	Expt. 187. P = 1. t.	0.4343 k.		Expt. 189. P = 1. t.	0.4343 k.	Expt. 190. P = 1. t.	0.4343 k.
of 183 & 182	20.5	0.0043	20.5	0.0049	$Ir = \frac{1}{60000}$ [2]	20	0.0018	20	0.0018
	42	0.0050	40.5	0.0045	$NaOH = \frac{1}{220}$	49.5	0.0019	51	0.0019
	60	0.0062	60	0.0050	$H_2O_2 = \frac{1}{30}$	93.5	0.0020	104.5	0.0022
	$61 = t_{A/2}$		$60 = t_{A/2}$			147.0	0.0022		

$Ir = \frac{1}{60,000}$	Expt. 191. P = 1. t.	0.4343 k.	Expt. 192. P = 1. t.	0.4343 k.	$Ir = \frac{1}{60,000}$	Expt. 193. P = 1. t.	0.4343 k.	Expt. 194. P = 1. t.	0.4343 k.
$NaOH = \frac{1}{55}$	20	0.0023	20	0.0024	$NaOH = \frac{2}{55}$	20	0.0021	20	0.0021
$H_2O_2 = \frac{1}{30}$	40	0.0025	40	0.0026	$H_2O_2 = \frac{1}{30}$	50	0.0021	50	0.0021
	85	0.0025	80	0.0026		80.5	0.0020	80	0.0021
	169	0.0028	166	0.0028					

Experiments with Colloidal Silver under Pressure.—MacIntosh[3] measured the rate of decomposition of hydrogen peroxide by colloidal silver and found that the constant calculated from the equation for first-order reactions decreased, whereas it increases in the case of gold, platinum, etc. He explains this phenomenon by assuming that colloidal silver is slowly dissolved by hydrogen peroxide. The author's experiments verify MacIntosh's results. It was found necessary to work in dilute alkaline solutions because the silver dissolved very rapidly even in neutral solutions of hydrogen peroxide. For instance, the decomposition of a $\frac{M}{15}$ solution of hydrogen peroxide by a $\frac{1}{20,000}$ gram atom solution of colloidal silver became immeasurably slow after 20 minutes.

[1] Professor Bredig has very kindly informed the author that subsequent investigation in his laboratory has shown that the method of analysis employed here for iridium gives faulty results. These figures do not, therefore represent the true concentrations.

[2] Partly coagulated.

[3] J. Phys. Chem., 6, 15.

TABLE 8.

	Expt. 221. P = 60.		Expt. 222. P = 1.			Expt. 223. P = 60.		Expt. 224. P = 1.	
ons.	t.	0.4343 k.	t.	0.4343 k.	Concentrations.	t.	0.4343 k.	t.	0.4343 k.
0	7	..	7	..	$Ag = \frac{1}{50,000}$	5.5	..	5	...
$\frac{1}{10}$	17	0.0189	17	0.0181	$NaOH = \frac{1}{200}$	15.5	0.0128	15.5	0.0135
	37.5	0.0165	40	0 0151	$H_2O_2 = \frac{1}{40}$	36.5	0.0094	35.0	0.0128
	77	0.0126	103	0.0119		75.5	0.0088	75	0.0117
	Expt. 225. P = 1.		Expt. 226. P = 50.						
$\frac{1}{50}$	5	..	6.5	..					
	16.5	0.0111	16.0	0.0146					
	36.5	0.0101	36	0.0118					
	76.5	0.0076	76	0.0097					

Theoretical Considerations.

make the reasonably safe assumption that the reaction takes a heterogeneous system let us consider under what conditions gen concentrations would appreciably affect the catalysis.

e the reaction under pressure goes completely as far as we can e by ordinary analytical means, any chemical equilibrium be- ydrogen peroxide, oxygen and water may be left out of con- n. It has been suggested by several authors that the oxygen intermediate compound with the metal or, perhaps, a solid Neither of these hypotheses preclude the existence of a layer sed oxygen on the surface of the solid phase.

se, then, the first step of the reaction is represented by the equa-

$$\text{I.} \qquad yO + nM = M_nO_y,$$

$_nO_y$ is either a *chemical* compound or a solid solution and that is followed by a second according to the equation

$$\text{II.} \quad M_nO_y + yH_2O_2 = nM + yO_2 + yH_2O.$$

and Brunner[1] have shown that the measured rate will be affected te of the *chemical* reaction in heterogeneous systems only when r is slow in comparison to the rate of diffusion of the substance ng decomposition. In the light of these considerations, pressure ve an effect on the measured rate of reaction when:

e activity of the platinum-oxygen phase in the second step of ion changes with increasing concentration of oxygen.

e rate with which the chemical compound or solid solution M_nO_y st step of the reaction is formed, varies with the concentration

[1] ysik. Chem., 51, 95 and 494.

of the oxygen. As the experimental results given in this article prove definitely that pressure has no measurable effect on the rate, we are forced to conclude either, that the two above cases do not exist, or that the chemical reactions are rapid in comparison to the rate of diffusion of the hydrogen peroxide. The latter hypothesis agrees very well with the experimental results obtained by J. Teletow.[1]

Pressure would also have no appreciable effect on the reaction if an active platinum compound were formed directly from the union of platinum and hydrogen peroxide and not from platinum and oxygen, even if the rate of union were *not* rapid.

Summary.

The chief results of this article are: A method has been worked out whereby rates of reaction may be measured under high gas pressure.

It has been experimentally determined that the catalytic decomposition of hydrogen peroxide by colloidal solutions of platinum, palladium, iridium, gold and silver is unappreciably affected by increasing the pressure of oxygen gas above the reaction mixture from 1 to 200 atmospheres.

This investigation was carried out in the chemical laboratory of the University of Heidelberg during the years 1905–6, under the direction of Prof. Bredig to whom my sincere thanks are due for friendly and valuable advice.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
October 9, 1907.

A METHOD FOR THE SEPARATION OF IRON FROM INDIUM.

BY F. C. MATHERS.

Received December 16, 1907.

One of the most difficult steps in the purification of indium is its separation from iron. Winkler[2] obtained a separation by the fractional precipitation of the sulphide, the indium sulphide being less soluble than the iron sulphide. A more satisfactory method was devised by Bayer,[3] who treated a solution of the mixed chlorides with sodium sulphite. Basic indium sulphite is precipitated from this solution upon boiling. The precipitate, after filtration, was dissolved in a solution of sulphurous acid and basic indium sulphite was again precipitated by boiling. This solution and reprecipitation was repeated several times to completely purify the indium. The Bayer method was tested in this laboratory, but gave unsatisfactory results. Weselsky[4] treated the chlorides of indium and iron with sulphur dioxide or sodium thiosulphate and then

[1] Dissert., Heidelberg, 1906.
[2] J. pr. Chem., 94, 1 (1865).
[3] Bayer, Lieb. Ann., 158, 372 (1871).
[4] J. pr. Chem., 94, 443 (1865).

ith barium carbonate, which precipitated indium hydroxide, together ith traces of iron and zinc. Meyer[1] treated the material that contained dium and iron with sodium carbonate until neutral and then with a lution of potassium cyanide until the precipitate that first formed as redissolved. The solution thus formed was diluted with 10 volumes water and was boiled. This decomposed the potassium indium cyan- e and indium hydroxide was precipitated while the iron remained in solu- on as potassium ferri- or ferrocyanide. This method was found, upon ial, to give fair results. The indium, however, is not completely pre- pitated by boiling, considerable amounts of it being found in the fil- ate. The precipitate is very gelatinous, difficult to wash, and often isses through the filter paper before the washing is completed. For ese reasons the method is not satisfactory. Some quantitative results tained in this laboratory with the Weselsky method follow:

Indium oxide present.	Indium oxide precipitated by dilution and boiling.	Indium oxide precipitated from the filtrate with ammonium hydroxide.
0.0320 gram	.....	0.0022 gram or 6.8%
0.0545 gram	0.0528 gram or 96.8%	0.0014 gram or 2.5%

Dennis and Geer[2] have proposed the removal of the iron by extracting e ferric sulphocyanate with ether. This method has been applied to e removal of iron from nickel, cobalt, copper, aluminum, etc. Indium lphocyanate, however, is quite soluble in ether and for this reason dium is always present with the iron in the ether extract. The labor volved in recovering the indium thus dissolved constitutes a serious awback in this method, which is otherwise very satisfactory and yields indium that is free from iron.

Several other methods have been suggested for the separation of iron d indium, but those cited above seem to have been the ones most gen- ally used and to have been the most satisfactory.

The method here proposed for the removal of iron from indium is the ecipitation of iron from nitroso-β-naphthol. This reagent[3] quanti- tively precipitates cobalt, copper, and iron, but does not precipitate uminum, lead, zinc, or nickel. Experiment showed that indium also as not precipitated, and this led to the development of the following ethod of separation:

A solution of the indium chloride or sulphate containing a small quan- y of iron was evaporated to a volume of 20 to 25 cc., was neutralized ith ammonium hydroxide and then an equal volume of 50 per cent. etic acid was added. The iron in these solutions was precipitated ith nitroso-β-naphthol dissolved in 50 per cent. acetic acid. The solu-

[1] Meyer, Lieb. Ann., 150, 137 (1869).

[2] This Journal, 26, 437 (1904).

[3] Ilinski and Knorre, Ber., 18, 2728 (1885); Knorre, Ber., 20, 283 (1887).

tion may be either hot or cold when precipitated, but it should stand several hours before filtering, and should be cold when filtered. The residue is washed with 50 per cent. acetic acid and finally with water. Before using this method the bulk of the iron must be removed by some other method. Since the precipitate of iron with nitroso-β-naphthol is very bulky, 0.05 gram of iron is about the maximum quantity that can easily be handled on a 12 cm. filter paper. The indium precipitated by electrolysis from a solution containing indium sulphate and quite large amounts of ferric sulphate and strongly acidulated with sulphuric acid, contains only small amounts of iron. This metal can then easily be freed from the iron that it still contains by precipitating the iron with nitroso-β-naphthol. Colorimetric analysis of the indium, after the precipitation of the iron by this method, showed that the content of iron was very low. This small amount of iron[1] could easily have been introduced into the solution during evaporation by the dust from the air. Quantitative determinations of the iron remaining in the indium gave the following results:

Indium oxide taken. Gram.	Ferric oxide added. Gram.	Nitroso-β naphthol used. Gram.	Ferric oxide still present in the indium oxide. Gram.
0.3148	0.0328	5.0	Less than 0.00005
0.1738	0.0262	4.0	" " 0.00005
0.2184	0.0197	3.0	" " 0.00005
0.3061	0.0262	2.5	" " 0.0001
0.2142	0.0262	2.5	Very faint red

Some indium remains in the residue with the iron and a second precipitation will not remove all of it. The indium in these residues can easily be detected with the spectroscope. The total quantity of indium that is lost in these iron residues is, however, quite small, as is shown by the following data:

Indium oxide taken. Gram.	Ferric oxide added. Gram.	Ferric oxide obtained from First precipitation. Gram.	Ferric oxide obtained from Second precipitation. Gram.	Indium oxide in ferric oxide in First precipitation. Gram.	Indium oxide in ferric oxide in Second precipitation. Gram.
0.3061	0.0262	0.0286	0.0273	0.0024	0.0011
0.1520	0.0262	0.0283	0.0273	0.0021	0.0011
0.2142	0.0262	0.0281	0.0266	0.0019	0.0004

CORNELL UNIVERSITY,
December, 1907.

SOME NEW COMPOUNDS OF INDIUM.

BY F. C. MATHERS AND C. G. SCHLUEDERBERG.

Received December 16, 1907.

This paper describes the preparation and properties of four new compounds of indium: the perchlorate, the iodate, the selenate, and the caesium-selenium alum.

[1] Stokes and Cain, This Journal, 29, 409 (1907).

kium Perchlorate, $In(ClO_4)_3.8H_2O$.—Metallic indium was dissolved ute perchloric acid. This solution was evaporated upon a hot plate concentration such that when cooled in a mixture of ice and salt, crystals were formed. The beaker was then placed in a vacuum ator containing concentrated sulphuric acid where the crystallizacontinued in a satisfactory manner. The crystals were rapidly l with a small amount of water, dried on filter paper, and then placed : vacuum desiccator for a short time.

: metallic indium that was used had been deposited electrolytically hen fused in a charcoal crucible in a current of hydrogen. This ı was necessary to remove salts that were occluded from the elec- e. The perchloric acid that was used was purchased from Schuck- . It contained a small quantity of sulphuric acid, which was re- d by the addition of the proper amount of barium hydroxide.

o different methods were used to determine the indium in the indium lorate. The shorter procedure consists in heating the sample to ıperature of about 200°, at which decomposition of the perchlorate place, then evaporating with nitric acid, and finally igniting the e to the oxide. In the other method the indium is precipitated : hydroxide with ammonium hydroxide and is weighed as the oxide. econd method is preferable, since it permits determinations of both ıdium and the chlorine (ClO_4) in the same sample. To determine hlorine, the filtrate from the indium hydroxide was treated with cess of sodium carbonate and a few drops of potassium permangan- It was then evaporated to dryness on a water-bath and heated to fusion, this treatment decomposing the perchlorate and yielding a de. The mass was dissolved in dilute nitric acid and the solution reed from the insoluble manganese dioxide by filtration. The chlor- ı the filtrate was precipitated and weighed as silver chloride.

	Theory for $In(ClO_4)_3.8H_2O$. Per cent.	Found. Per cent.			
Indium oxide	24.92	24.82	; 24.73	; 24.83[1]	
Chlorine	19.08	19.05	; 18.67	;	

empts to make direct determinations of the water were unsuccess- ı account of decomposition and the formation of a basic salt with of chlorine. Samples of the crystals that had been dried for several in the vacuum desiccator gave higher values for the indium oxide, ınd 25.7. These values agree with the theory for $In(ClO_4)_3.7H_2O$. s evidently due to the loss of water of crystallization, since several ent samples that were dried for only a few minutes gave results howed 8 molecules of water.

ium perchlorate is a colorless, crystalline, deliquescent compound

[1] Determined by Method 1.

that is soluble in water and in absolute alcohol, but much less soluble in ether. It easily forms saturated solutions in water. Basic salts are precipitated from a neutral water solution when the temperature is raised to 40°. When heated in the open air, the crystals fuse at about 80°, but do not form a clear liquid. When the heating is carried to a higher temperature, but not to a red heat, the substance decomposes with a liberation of chlorine. The residue is insoluble in water, but is easily soluble in dilute nitric acid, and this solution gives a strong test for chlorine.

Indium Iodate, $In(IO_3)_3$.—Anhydrous indium trichloride was prepared and sealed off in a glass tube by a method previously described.[1] Potassium iodate was recrystallized twice from water. This sample was analyzed by treating it with dilute sulphuric acid and potassium iodide and titrating the iodine that was liberated. Taken, 0.0750 g. KIO_3; found, 0.0749 g.

Equivalent quantities of the indium trichloride and of potassium iodate were dissolved separately and then mixed. A precipitate formed immediately but it showed no crystalline structure when examined with a microscope. The entire solution was evaporated to dryness upon a water-bath and the residue was collected upon a Gooch crucible and was thoroughly washed with cold water.[2] The crucible and contents were dried over sulphuric acid in a vacuum desiccator. Analyses of several samples prepared in this way did not give constant results. The substance was then dissolved in boiling nitric acid (1:10 by volume). On evaporation of this solution, the indium iodate separated in imperfect, broken crystals whose crystal system could not be determined. These crystals were washed with water and dried in a vacuum desiccator. The results of the analyses were as follows:

	Theory for $In(IO_3)_3$. Per cent.	Found. Per cent.
Indium oxide	21.71	21.76 and 21.93
Iodine	59.53	59.19 and 59.30
Water at 125°	0.08	
Loss at 160° (decomposition, brown color)		0.40

The indium was precipitated as the hydroxide with ammonium hydroxide and was weighed as the oxide. The iodine was calculated from the titration with sodium thiosulphate of the iodine that was liberated when a sample was treated with potassium iodide and dilute sulphuric acid.

Indium iodate is a white, crystalline, anhydrous compound. It is soluble in 1500 parts of water at 20° and in 150 parts of 1:5 nitric acid

[1] Mathers, This Journal, 29, 485 (1907).

[2] This is the method employed in his research upon iodates by A. Ditte, Ann. chim. phys. (6), 21, 145 (1890).

All attempts to grow large crystals from these solutions were ssful. It is soluble in dilute sulphuric acid and in hydrochloric ıt the latter causes a decomposition with the liberation of chlor- he crystals decrepitate when heated with a free flame, become in color and give off iodine vapor. If touched with a red-hot ey explode and form a cloud of iodine vapor.

m Selenate, $In_2(SeO_4)_3.10H_2O$.—Indium selenate was prepared lving indium hydroxide in selenic acid, which had been made ac- to the following method:

dust known to be rich in selenium was heated in a porcelain dish strong solution of potassium cyanide for several hours. On ;, a clear, amber-colored solution of potassium selenocyanate, e), was obtained. A current of filtered air was passed through ution for several hours in order to separate any tellurium that have been dissolved with the selenium. A small quantity of a olored precipitate that separated was filtered off. The filtrate oled to about zero degrees and cold, 50 per cent. hydrochloric ıfficient to entirely precipitate the selenium, was added, care be- en to add the hydrochloric acid slowly to avoid an appreciable emperature. The selenium is thrown down as a bright red, amor- precipitate, which was filtered off and thoroughly washed. This lissolved in a ten per cent. solution of potassium cyanide, treated r, precipitated in the cold as before, filtered off, washed very thor- and dried.

selenium was then dissolved in concentrated nitric acid and the ı evaporated to dryness on the water-bath, redissolved in very hydrochloric acid and again evaporated to dryness. The sele- ioxide thus obtained was dissolved in a little water and added to : water, through which a stream of chlorine was allowed to bub- us oxidizing the selenium dioxide to selenic acid. After being eated for several hours with chlorine the liquid was freed as far ible from excess of that gas by passing through it a current of

solution of selenic acid was neutralized with copper carbonate shly precipitated copper hydroxide. The blue solution of copper : thus obtained was filtered, concentrated on the water-bath aside to crystallize. Blue triclinic crystals of copper selenate ed. These were recrystallized from water solution and again :d in water and the solution freed from copper by electrolyzing atinum dish at low current density.[1] Electrolysis was continued o test for copper could be obtained with either ammonium hy- ·, potassium sulphocyanate or potassium ferrocyanide in small

[1] Metzner, Compt. rend., 127, 54 (1898).

portions of the solution. The solution of pure selenic acid thus obtained was treated with indium hydroxide. Indium selenate crystallized out in white, easily soluble, hygroscopic crystals. Analysis gave the following results:

	Theory for $In_2(SeO_4)_3.10H_2O$. Per cent.	Found. Per cent.
Indium oxide	33.08	32.9 – 33.0
Selenium	28.30	28.3 – 28.2

Indium Caesium Selenate, $CsIn(SeO_4)_2.12H_2O$.—Caesium-indium-selenate, the alum, was made by crystallizing a solution of caesium selenate (prepared from caesium hydroxide and selenic acid) and indium selenate.

The alum crystallizes in beautiful colorless octahedra, belonging to the tetragonal system, which are soluble in water, efflorescent in the air and are of the following composition:

	Theory for $CsIn(SeO_4)_2.12H_2O$. Per cent.	Found. Per cent.
Selenium	21.18	21.04
Indium	15.3	15.5
Caesium	17.7	17.8

In the above analyses the selenium was determined by repeated precipitation with sulphur dioxide gas from a hot dilute solution of the salt. The precipitate was collected on a Gooch filter, and the filtrate was boiled down and again treated with sulphur dioxide. It was found necessary to repeat this operation several times in order to remove all of the selenium from the solution. The Gooch filter was dried at 102–5° and the selenium was weighed.

The indium was precipitated by ammonium hydroxide as the hydroxide from the hydrochloric acid solution of the salt, collected on an ashless filter, heated in a porcelain crucible and weighed as In_2O_3.

For the determination of the caesium, the selenium was first removed and the caesium was then precipitated from the chloride solution by chlorplatinic acid and weighed as caesium chlorplatinate.

Cornell University,
December, 1907.

A NEW FORM OF COLORIMETER.

By George Steiger.

Received November 6, 1907.

The many uses to which colorimeters can be put are too well known to need mention here.

Instruments using the principle upon which this one is based—the ratio of the thickness of the liquid through, and not the actual dilution to equal concentrations—are not applicable to all colorimetric determinations. It will be found, in comparing such a solution as is used in the colorimetric determination of manganese and some other substances,

that there is a change not only of the intensity of the color, but also of the color itself, making it impossible to find a point at which two solutions of different concentrations will have the same depth of tint. In some other cases, as for instance the yellow color of the higher titanium salts, this principle gives perfect satisfaction.

The instrument to be described consists of two wooden boxes, the interior portions of which are finished in dead black. In Fig. 1, AA is

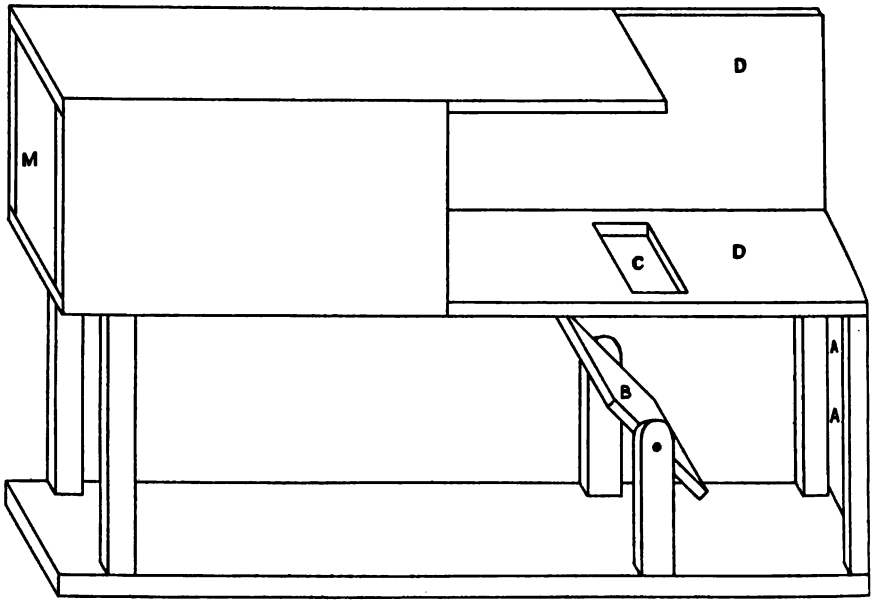


Fig. 1.

a piece of finely ground glass, and this should be illuminated with the full light of the sky. B is a mirror mounted to swing so that light may be thrown perpendicularly through the hole C.

The second portion of the apparatus consists of a box, as shown in Fig. 2, made with two parallel grooves in the bottom, in which the two glass cells, CC, can be moved back and forth, and the hole E, which admits light reflected by the mirror B of Fig. 1. These cells are about 15 cm. long, 2.5 cm. wide, and 5 cm. deep. On the bottom of each cell and near the outside edge is engraved a scale, a convenient unit for which is the millimeter. FF are glass tubes with mirrors, GG, attached to the lower ends at an angle of 45°. These tubes may be lifted up when it is desired to remove the cells, they may also be removed entirely from the clips RR for cleaning purposes, but they should be pushed down when in use so that the lower edges of the mirrors touch the bottoms of the cells. When ready for use this box is placed in the space marked DD, Fig. 1.

Care should be taken to place the mirrors at an exact angle of 45°.

Under these conditions, in each cell, all light coming through the bottom of the cell and reflected through the end K, will go through the same

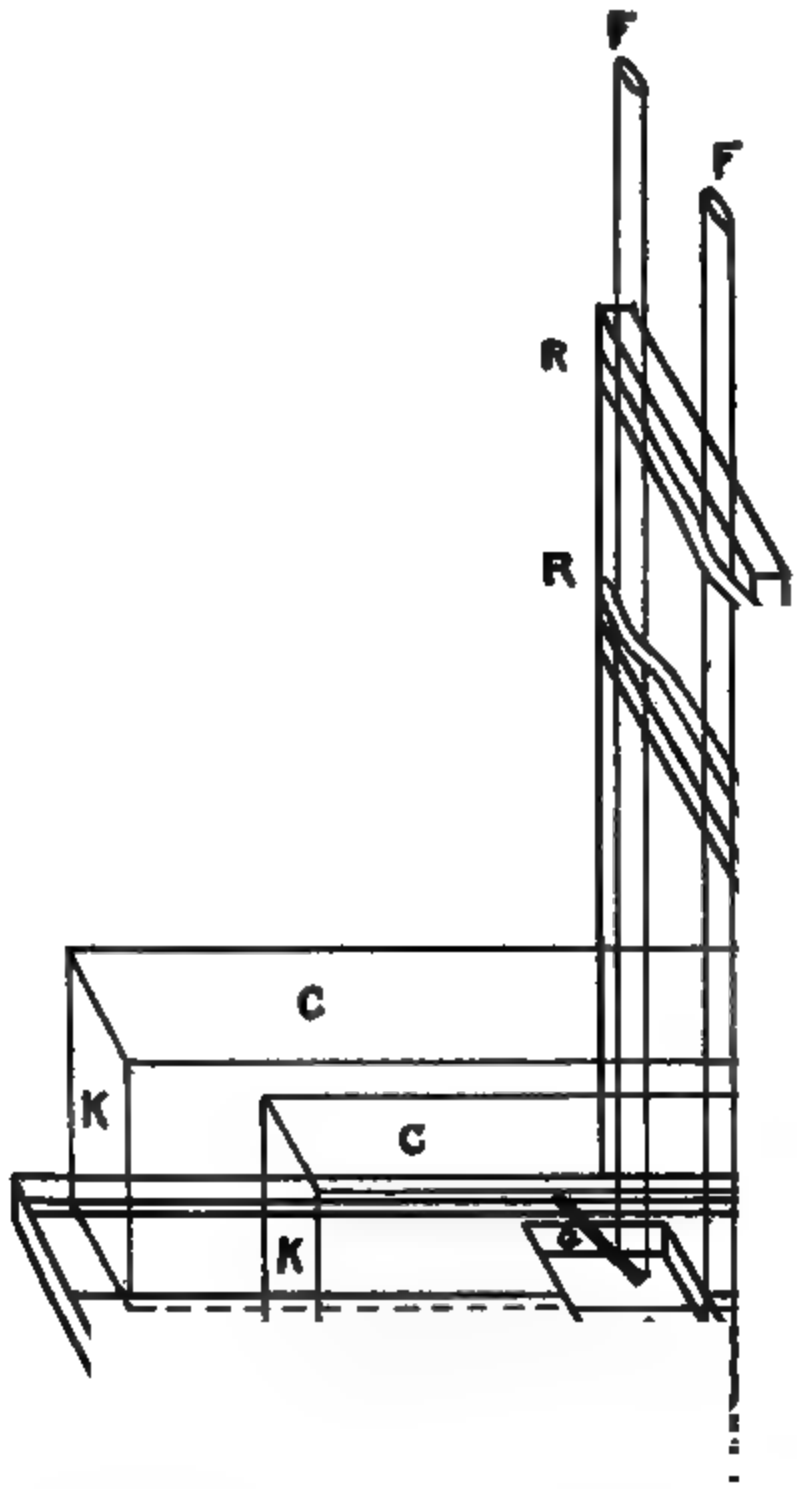


Fig. 2.

thickness of liquid, and if the mirror were a reflecting surface coming in direct contact with the liquid this distance would be represented by the line O P, Fig. 3. There is a small error here, due to the converging of the rays to the eye; this is so slight, however, as not to cause any perceptible uneven illumination.

The mirrors being made of ordinary looking glass, the reflecting surface will be the upper side G H G, Fig. 3, and the light must go through the glass of the mirror before striking the reflecting surface, and the same on leaving. The distance which the light travels through the glass of

e mirror will be represented by twice the length of the hypotenuse of isosceles-right-angle-triangle, the equal sides of which are each equal the thickness of the glass, and must be deducted from the length O P.

Fig. 3.

A ray of light entering the glass at the point marked N will travel to and then be reflected to *t*. From *t* to *w* it will go through the colori-etric solution, and this distance is therefore the length to be measured. point, H, is marked on the mirror near the outer edge, so that it may seen in the same line of vision as the scale on the bottom of the cell, d perpendicularly above *t*. In looking through the end K, this mark ll be recorded at the point *t′* directly below it on the scale, and *t′*P ing the same at *t w*, the distance desired can be read off. The posi-n of the point H is determined by measuring off, on the back of the rror, a distance from the lower edge equivalent to three times the ickness of the glass. It may be convenient, if thin looking glass has en used, to have this point farther up on the mirror (H′), in order that may be seen more plainly, but if so moved an addition must be made the observed reading, equivalent to one of the sides adjacent to the ght angle of an isosceles-right-angle-triangle, the hypotenuse of which equal to the distance this point has been removed from H. It is con-nient in making the graduation on the cell to allow for this correction. e reading can then be made directly.

Glass cells to answer the purpose may be had of any of the large sup-

ply houses, but not graduated, the graduation must be done in the laboratory. The supports F F can be made of rather heavy walled glass tubing, about 1 cm. outside diameter.

The mirrors are made of a good grade of looking glass, the lower and top edges blackened, and cemented to the ground ends of the glass tubes with Canada balsam, after which the backs are coated with paraffin. Paraffin answers well as a coating for a large number of colorimetric solutions. In case a liquid is to be used which attacks paraffin, a substitute must be employed which is unaffected by the liquid in question. It will be found necessary to replace the mirrors from time to time, as it is not possible to so protect the silvered surfaces as to prevent the gradual eating in from the edges by the various solutions used.

The comparison is made by pouring a solution of known strength into one of the cells. The unknown solution made up to a definite volume, is put into the other. The left-hand cell is then placed at a convenient point, which should be determined by the depth of color of the solution it contains. The right-hand cell is then moved back and forth till, on looking in the end M of the apparatus, Fig. 1, the two mirrors appear to be of the same shade.

The strengths of the two colorimetric solutions being inversely proportional to the thickness of the liquids looked through, by substituting in the following equation the amount of the material to be determined may be found.

Let R equal the reading of the cell containing the known solution with a concentration C, and r the reading of the cell containing the unknown solution, which has a concentration c, then

$$c = \frac{RC}{r}.$$

CHEMICAL LABORATORY,
U. S. GEOLOGICAL SURVEY,
October 31, 1907.

THE ESTIMATION OF SMALL AMOUNTS OF FLUORINE.

BY GEORGE STEIGER.

Received November 6, 1907.

The estimation of fluorine in such substances as rock mixtures, which require a carbonate fusion to bring the fluorine into a soluble form, is not only a long and difficult operation, but also the final results are far from being satisfactory.

When as much as one tenth of one per cent. is present, a negative result will often be obtained by the Berzelius method, the one usually employed.

The method to be described is based on the well known fact, that the presence of fluorine has a powerful bleaching effect on the yellow color,

which is produced by the oxidizing of a titanium solution with hydrogen peroxide. A solution of definite volume is made containing the fluorine to be estimated, also having a known amount of titanium present; this is compared in a colorimeter with a second solution containing an equivalent amount of titanium per cc., and the bleaching effect recorded. From the extent of this bleaching, the percentage of fluorine can be calculated.

Although the results obtained are not so accurate as those given by many methods for the estimation of other elements, yet considering the difficulty of the fluorine determination, and the time and labor required by methods now in use, the present one may well be employed, where small quantities of fluorine are to be determined. The operations require not only less skill to carry out, but are fewer in number and take much less time.

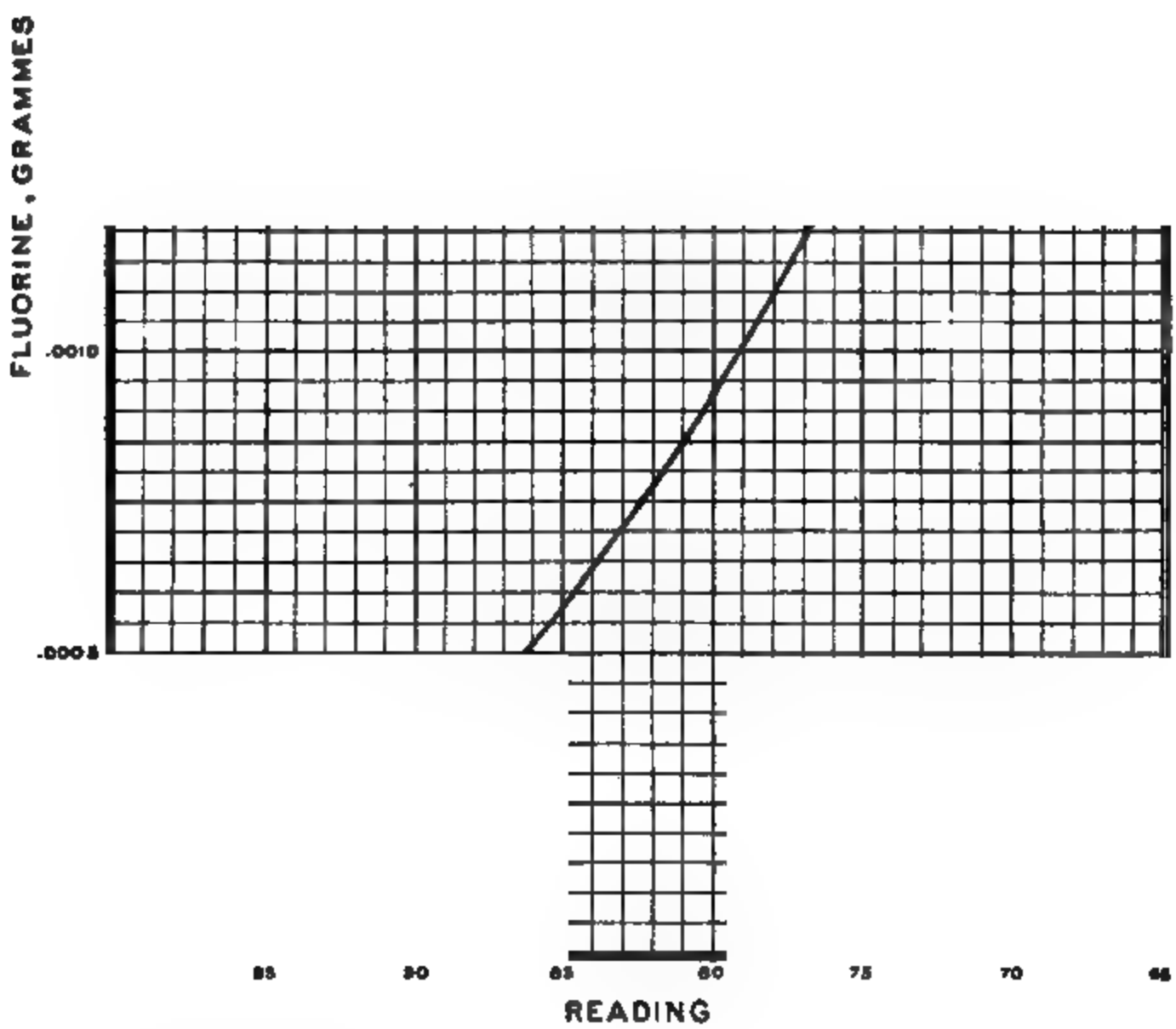
Traces of fluorine amounting to several hundredths of one per cent. are easily detected, and an approximation to the quantity can be made. In amounts up to a few tenths of a per cent. the method seems to be more reliable, and if not more than two per cent. is present, the results compare favorably in accuracy with the standard methods. It is hardly to be expected, however, to find a colorimetric method using only a few milligrams of the material to be determined, that will compare in accuracy with the gravimetric methods using much larger quantities, where considerable percentages of fluorine are concerned.

Description of the Method.—In rock mixtures containing only a few tenths of a per cent. of fluorine, two grams of the finely ground rock powder are fused with four or five times its weight of a mixture of sodium and potassium carbonates. It may be necessary in the case of a subsilicic rock, to add silica, 50 per cent. of which should be present.

From the aqueous leach of the fusion, all of the alumina, and most of the silica, are separated by adding ammonium carbonate, heating on the water bath for fifteen or twenty minutes, allowing to cool an hour or more and filtering. The filtrate is evaporated to small bulk (25 or 30 cc.) and filtered a second time to insure a perfectly clear solution, a condition absolutely necessary for a satisfactory comparison of the color. After this treatment the solution should be entirely free from alumina, and contain no more than 25 milligrams of silica. This amount of silica is not sufficient to interfere with the reaction.

The solution is now put into a 100 cc. measuring flask, sulphuric acid added to almost neutral reaction with care not to add an excess, and well shaken to free from the excess of carbon dioxide, and then fully acidified. Care should be taken not to have an excess of acid present before shaking, for the reason that the escaping gas will carry off some fluorine; even under the above conditions a slight loss occurs. If a con-

siderable amount of fluorine is present, an aliquot part of the solution should be used containing not more than 2 or 3 milligrams. 20 cc. of standard titanium sulphate solution[1] (1 cc. of which contains 0.0001



[1] Directions for the preparation of the titanium solution will be found in the second part of this paper.

gm. TiO_2) are now added, together with 2 or 3 cc. of hydrogen peroxide, and the flask filled to the mark with water. The solution is now ready to be compared with the standard. The latter is prepared by using 20 cc. of the standard titanium solution, 2 or 3 cc. of H_2O_2 and bringing the volume up to 100 cc. with water.

These two solutions containing the same amount of titanium per cc. should be of the same depth of color, but the one having the fluorine present will be found to be of a lighter shade, owing to the bleaching effect which that element has on a solution of titanium oxidized by H_2O_2. The extent of this bleaching is not directly proportional to the amount of fluorine present, but by reference to the curve below, the quantity corresponding to a given bleaching can be found.

The two solutions are now compared in a colorimeter and their ratio recorded. Suppose a ratio for example, of 100 to 85, that is, the fluorine present has caused a bleaching of the solution equivalent to 15 per cent. of the titanium present; then by finding the point on the abscissa marked 85, with the help of the curve the amount of fluorine (0.00055) can be directly read off on the ordinate.

It is necessary to employ a colorimeter[1] whose error is not more than two or three per cent.

Experimental Work.

Directions for the preparation of the solutions used in the experimental part of this work:

Titanium Solution.—A quantity of potassium-titanium-fluoride was dissolved in water, a large excess of sulphuric acid added and the solution evaporated till fumes of sulphur trioxide came off, then cooled, more water added and the operation repeated. This was done several times to insure the entire removal of fluorine; the solution was then largely diluted with water, and its contents of titanium determined by precipitating a portion of it with ammonia, and weighing the titanium directly as its oxide. The solution was next so diluted as to contain 0.0001 g. TiO_2 per cc., at the same time adding enough sulphuric acid to make a 3 per cent. solution.

Fluorine Solution.—1.236 gm. of potassium-zirconium-fluoride were dissolved in one liter of water. One cc. of this solution contained 0.0005 gm. of F.

Silica Solution.—Five grams of silica and 10 gm. of sodium carbonate were fused together, dissolved in water, filtered, and made up to 500 cc. This solution contained 0.01 gm. SiO_2 per cc.

Aluminum Solution.—Common alum was dissolved in water sufficient to make a solution containing 0.01 gm. Al_2O_3 per cc.

[1] A description of the colorimeter used in this work will be found in the preceding article.

Phosphorus Solution.—A solution of microcosmic salt was made, one cc. of which contained 0.005 gm. P_2O_5.

Iron Solution.—A solution of ferric sulphate containing 0.005 gm. Fe in each cc.

In the method described, after fusing the rock with carbonates and leaching with water, there will be in solution besides the fluorine, silicates and aluminates of sodium and potassium, and the excess of sodium and potassium carbonates, all in large amounts, a small quantity of iron, and all of the phosphorus, chlorine, vanadium, and some other elements usually found in very small quantities. The effect of silicon, aluminum, sodium, and iron salts, and the phosphorus, has been determined; the possible effect of traces of such salts as vanadates, tungstates, and chlorides, has not.

In all the following experiments 20 cc. of the titanium solution and 1½ cc. of the fluorine solution were used, oxidized with 2 or 3 cc. of hydrogen peroxide and made up to 100 cc. A large number of comparisons were made of this solution with one of the same composition, excepting that it contained no fluorine. The average ratio found was 100 to 82.5, that is, 1½ cc. of fluorine solution (0.00075 g. F) should cause a bleaching effect equivalent to 17.5 per cent. of the titanium present, when the solution contains no interfering substances.

The following results were obtained, when the several salts were introduced into solutions containing the above quantities of titanium and fluorine.

The figures given under the head of "reading" denote the ratio of the color of the solution containing the fluorine, etc., to that of the standard titanium solution, the latter being taken as 100.

Effect of Sodium Salts.—The sodium carbonate was dissolved in water, the solution acidified with sulphuric acid and well shaken to free it from dissolved gas, the titanium, fluorine, and hydrogen proxide added, and made up to 100 cc. with water.

Na_2CO_3, gms.	8.	8.	8.	8.	8.	8.
Reading	85.2	85.7	83.7	86.4	85.2	84.4
Na_2CO_3, gms.	8.	8.	8.	8.	8.	8.
Reading	82.9	83.5	83.3	83.4	83.1	86.3
Effect of Silica.—						
Silica solution, cc. added		1.	2.	5.	5.	5.
Reading		84.4	83.3	83.8	85.7	84.2
Silica solution, cc. added		5.	10.	30.	50.	....
Reading		84.2	84.9	85.9	88.8	....
Effect of Aluminum.—						
Alum solution, cc. added		1.	3.	5.	5.	20.
Reading		92.	96.3	97.3	96.6	99.3

Effect of Iron.—

Iron solution, cc. added	5.	5.	....	....	....
Reading	90.	89.9	....	....	....

Effect of Phosphorus.—

P_2O_5 solution, cc. added	5.	25.	....	....	....
Reading	84.5	80.3	....	....	....

The following experiments were made having phosphorus present but no fluorine.

P_2O_5 solution, cc. added	5.	25.	....	....	....
Reading	98.4	94.3	....	....	....

This bleaching effect on the color of an oxidized titanium solution by phosphorus has been observed before.

These results show that sodium salts in large amounts have a slight effect in making the observed reading higher, but not enough to seriously alter the results. Silica in amounts up to 0.1 g. has but little effect. It is easy, however, by one precipitation with ammonium carbonate to leave not more than 30 milligrams of silica in solution. Aluminum, even in small quantities, has a very marked effect on the bleaching, but this base is entirely separated by the ammonium carbonate treatment. Phosphoric acid has the same effect as fluorine in bleaching the color, but as this is present in much smaller quantities than those used in the above experiments, its effect can be neglected. Iron prevents the bleaching, but as the quantity coming out in the leach water is hardly more than a trace, and even this small amount is probably separated by the treatment with ammonium carbonate it can also be neglected.

Various mixtures were made roughly representing commonly occurring rock mixtures, containing accurately known amounts of fluorine. Results of the fluorine determinations in these mixtures follow:

SiO_2.	Al_2O_3.	Fe_2O_3.	$MgCO_3$.	$CaCO_3$.	$NaHNH_4PO_4$.	TiO_2.	F calculated.	F found.
0.60	0.20	0.05	0.03	0.05	....	.....	0.0114	0.0102 Gm.
"	"	"	"	"	0.01	0.008	0.0052	0.00525 "
"	"	"	"	0.10	"	0.01	0.00284	0.0027 "
[1] 0.70	0.15	0.05	0.05	0.05	"	0.005	0.0005	0.0003 "
"	"	"	"	"	"	"	0.00526	0.0056 "
"	"	"	"	"	"	"	0.00526	0.0040 "
"	"	"	"	"	"	"	0.00253	0.0020 "
"	"	"	"	"	"	"	0.01228	0.0089 "
"	"	"	"	"	"	"	0.00516	0.00486 "
"	"	"	"	"	"	"	0.00536	0.00530 "

To give an idea of the amount of silica in solution after the treatment with ammonium carbonate, several determinations were made in the above solutions after the colors had been compared. The results follow:

[1] In this determination the fusion of the mixture was made as usual, and the fluorine added to the leach water before the treatment with ammonium carbonate.

SiO_2 0.0244 0.0740[1] 0.0268 0.0555[1] 0.0159 0.0298 0.0174 0.0113 0.0263 Gm.

The following determinations were made of fluorine in natural rocks and compared with the gravimetric results:

Gravimetric determination	0.15	3.01	3.01 per cent.
Colorimetric determination	0.21	2.58	3.20 per cent.

A number of determinations of fluorine were made in rocks containing quantities varying from 10 to 20 per cent., but the results were not satisfactory, being several per cent. out of the way.

CHEMICAL LABORATORY,
U. S. GEOLOGICAL SURVEY,
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VOLUMETRIC METHOD FOR THE DETERMINATION OF ZINC.

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Several schemes have been advanced for the estimation of zinc by titration with potassium ferrocyanide, but so far no one of them has found universal application. The methods which have found favor are either so complicated or so difficult in manipulation that a large personal error is always introduced and it seldom happens that very close checks are obtained by different operators, even when the same procedure is followed. Nearly a year ago I became interested in the volumetric determination of this metal with the idea of substituting it for the rather tedious gravimetric method which has always been in use in our laboratory.

At first, and for quite a long time in fact, I was not very successful and encountered numerous difficulties. The samples which I used in this preliminary work were spelters, the zinc content of which had been very carefully determined by difference. Finally, after a trial of all the methods which seemed reliable, with varying successes, I concluded that changes might be made to good advantage in nearly all of them, so with what experience I had already gained, I attempted to work up a scheme which would embody the good points of all of these methods and as far as possible none of the bad ones. The method which I am about to describe, therefore, is not new, but is rather a re-modeling of the older ones. The scheme is one which is identical in certain parts for almost every condition, but there are some slight variations which are necessary for different products and, if accuracy is desired, they should be observed. Accordingly, I will describe the method, applying it to typical cases.

Preparation of the Ferrocyanide Solution.—Dissolve crystals of c. p. potassium ferrocyanide in water in the proportion of 22 grams to the liter. If the solution is not clear, it should be filtered before it is diluted to the desired volume. It is a good plan to make up several liters at a

[1] In these two cases the silica was filtered immediately after being precipitated with ammonium carbonate, which accounts for the large quantity found.

time, as the solution remains constant almost indefinitely, and if many determinations are necessary, a bottle of fifteen, or even twenty, liters of solution will not last very long.

Preparation of the Standard Zinc Solution.—This solution should be made up with the greatest care, as all subsequent work depends on its accuracy. In order to make up two liters, weigh very carefully and transfer to an 800 cc. beaker 10 grams of c. p. zinc or an equivalent weight of the oxide (12.4465 grams) -if the latter is used, it must be freshly ignited, cooled in a desiccator—and dissolved in 50 cc. of hydrochloric acid diluted with water. Heat until solution is complete and then dilute to about 300 cc. and add a considerable excess of bromine water. Heat until the bromine is entirely expelled. Wash the cover glass and the sides of the beaker and add an excess of ammonia. Put in a warm place on the hot plate where it will remain just below the boiling-point, or boil very gently for about fifteen minutes. By this time the small amount of iron, which is nearly always present, should be completely precipitated. Filter carefully into a graduated liter flask, washing the beaker and precipitate once with water containing a little ammonia and then several times with hot water. Replace the flask under the funnel by a small beaker (about 250 cc. capacity) and dissolve the iron precipitate in hot dilute hydrochloric acid. Re-precipitate the iron with ammonia and filter again, adding the filtrate to the main solution. Burn the filter paper containing the iron precipitate and ignite. Weigh as Fe_2O_3 and calculate to Fe, deducting this weight from the original 10 grams of zinc. Sometimes small amounts of silica and dirt are also present in the so-called c. p. zinc, and the weight of this should also be deducted. These are small corrections and make very little difference as a rule, but it is always well to make them, as it gives the operator more confidence in his results and leaves no loop-hole for inaccuracy in later work. Now make the solution barely acid, using a small piece of litmus paper as an indicator and add 30 cc. of hydrochloric acid in excess for each liter of solution. Add also 10 grams of ammonium chloride for each liter. Dilute to the mark with water, after cooling, and pour carefully into a *dry* two-liter bottle. Do not wash out the flask, but after it has drained as much as it will, fill it to the mark with distilled water and add this to the rest of the solution. Shake until thoroughly mixed and the solution is ready for use. Its value will be 0.0050 gram of zinc per cc. of solution—less a small correction due to the impurities deducted from the original weight.

Standardization.—By means of standard pipettes, measure out three portions of the zinc solution of 20 cc. each, three portions of 50 cc., three of 70 cc., and three of 100 cc., into 400 cc. beakers of the wide shallow type, which will greatly lessen the amount of stirring necessary in order

to obtain a homogeneous solution after each addition of the ferrocyanide. Add about 1 cc. of hydrochloric acid to each of the smaller portions. Dilute each to 150 cc. and all are ready for the titration. Except for very accurate work it is not necessary to take more than three or four portions altogether (one for each amount) to determine the average value of the ferrocyanide solution, but it has been found[1] that a slightly different factor should be used for different amounts of zinc, hence the necessity in accurate work for establishing these factors for amounts of solution likely to be used most frequently. Fill a clean burette with ferrocyanide, heat one of the portions of zinc chloride nearly to boiling and titrate as follows: Pour off about 20 cc. of the hot zinc solution into a small beaker and set it aside. Titrate the remainder by running in ferrocyanide, a few cc. at a time, until a drop tested on a porcelain tile with a drop of a five per cent. solution of uranium acetate shows a decidedly brown color. Now add all but about 2 cc. of the reserved portion, and having tested to be sure that the endpoint is not now overstepped, add the ferrocyanide in portions of half a cc. at a time until the end point is again passed. Finally add the last of the reserved portion, washing it all out with distilled water and carefully washing down the sides of the titration beaker, and finish the titration by adding two drops at a time, testing after each addition. The endpoint at this time will be sharper if instead of one drop two or three drops are added to the drop of uranium acetate on the tile. The amount of zinc lost at this stage of the titration will be so small as to be insignificant. When the final distinctly brown tinge is obtained, wait a minute and observe if one or more of the preceding tests do not also develop a color. Note the number of spots by which the endpoint has been overstepped, and since each test means an addition of two drops, or 0.1 cc. of solution, make the necessary correction when reading the burette. A blank should also be made and the final reading and all other readings corrected by this amount. The blank should be made with a solution containing 10 cc. of hydrochloric acid, neutralized with ammonia, made acid again, and after 3 cc. of acid have been added in excess, diluted to 150 cc. and heated nearly to boiling. This will usually require about 0.2 cc. to give a decided test. Run all the titrations in the same way and calculate the values for one cc. of the solution for the different portions, taking the average of the three results in each case if they are close enough (it is easy to obtain checks within 0.1 cc.), thus obtaining the different factors for the varying amounts of zinc—or what is equivalent to the same thing, for varying amounts of ferrocyanide. In actual work later, the factor should be used for the amount of solution which corresponds most nearly to that required for the titration. Ordinarily, however, the one average

[1] This Journal, 29, 205.

ɔr for three or four different amounts of zinc will be accurate enough .ll determinations.

ıe last solution which I standardized had the following factors:

Standard nc solution.	Grams of zinc.	Ferrocyanide solution.	Factors.
20	0.09995	19.4	0.005152
. 50	0.24988	48.1	0.005195
70	0.34983	67.2	0 005206
100	0.49975	95.5	0.005233

reater accuracy could be obtained with a slightly weaker solution, 15 or 18 grams to the liter, but for general application I find a solu- of the above strength the most convenient.

etermination of Zinc in a Spelter.—Method of sampling.—There are ral methods in common use, but probably the most accurate one break off small pieces from slabs in different parts of the pile until ıgh has been obtained to make a fair average—say five pounds for car load, if the shipment is homogeneous. The sample thus ob- ɜd should then be heated in an ordinary clay crucible until just melted, ı it should be poured into a wooden box, previously rubbed with k—and shaken violently. A box suitable for this must be made tight joints and no cracks and should be supplied with a cover. This :ment should result in a finely granulated sample. Screen out the ser pieces by passing through a 20-mesh and reduce the bulk of the stuff by coning and quartering until a small working sample is ob- ɜd. This not only will be found very easy to weigh, but will in ad- ın almost perfectly represent the whole consignment.

nalysis.—Weigh five grams of the sample of spelter, place in a 600 ɜaker, cover with a watch-glass and dissolve in 50 cc. of hydrochloric (1.20) diluted with water. Heat until completely dissolved. The ution of hydrogen, occasioned by the solution of the zinc, precipi- ; such metals as copper, lead and tin; but the heating should be con- ɜd until these metals go into solution again, as they occlude small unts of zinc. When solution is complete, neutralize with ammo- and reacidify with hydrochloric acid (1.20), adding 5 cc. in excess, .e to about 300 cc. and pass a current of hydrogen sulphide gas through warm solution for about twenty minutes. If the precipitated sul- es do not settle readily, allow the solution to stand for an hour or t a temperature just below the boiling-point. This will not be neces- , unless tin is present. Filter off the sulphides, allowing the filtrate ın into an 800 cc. beaker and wash the filter thoroughly with hot 'r. Heat the filtrate to gentle boiling and after the free hydrogen hide has been expelled add a large excess of bromine water and con- ɛ the boiling until the bromine has been expelled. Now add a large ss of ammonia and boil gently for about fifteen minutes. If the

amount of iron is considerable, it will not be necessary to boil so long, as it is only in the case of very small amounts that the precipitation is likely to be incomplete, unless the boiling is continued. Filter into a graduated liter flask, washing first with dilute ammonia—both the beaker and the filter—and then with hot water. Put about 10 cc. of hydrochloric acid (1.20) in the beaker, dilute with hot water and pour it over the precipitate on the paper, allowing it to run through into a small beaker of about 250 cc. capacity. Re-precipitate with ammonia and filter into the main solution in the flask, washing as before. If the amount of iron is very large, a third precipitation will be necessary, but in the ordinary spelter this is not the case. Put a small piece of litmus paper in the flask and add hydrochloric acid (1.20) until the solution is just acid, and then add 30 cc. in excess. Cool to room temperature and then make up to the mark with water. After mixing the solution thoroughly by several decantations back and forth from the flask to a beaker, measure out several portions of 100 cc. each (equivalent to 1/2 gram of spelter) by means of a pipette. I find it convenient to use a 400 cc. beaker for the titration. Usually only one portion is necessary, but it is well to have a second one in reserve. Dilute to 150 cc., heat nearly to boiling (about 85°) and titrate with ferrocyanide, as described in the procedure for standardization. Calculate the percentage of zinc by multiplying the standard value of one cc. by the number of cubic centimeters required (less the blank) and divide by 0.5, the weight of spelter taken as a sample.

If manganese is present in the spelter—a rare occurrence—the above result will be too high. If time is an object, the quickest way to overcome this difficulty is to make a separate determination of the manganese, although it may be removed before titration in a way I shall describe later. To determine the manganese, the best and most rapid way is to use the Bismuthate Method as applied to steels. Dissolve 1 gram of the spelter in a 150 cc. Erlenmeyer flask in 50 cc. of nitric acid (1 to 3) and boil off the nitrous fumes. Cool in ice-water and add about a gram of sodium bismuthate. If manganese is present, the pink color of permanganic acid will develop at once. If such is the case, filter through an asbestos filter into a 300 cc. Erlenmeyer, washing with 100 cc. of ice-cold 3 per cent. nitric acid. Add a measured amount of ferrous sulphate solution (12 grams to the liter) until the solution is perfectly colorless; titrate the excess with a standard permanganate solution (1 gram to the liter). Subtract the volume of permanganate required from the amount of the latter equivalent to the volume of ferrous sulphate used and multiply by the manganese value of the permanganate solution. The factor is about 0.00035 for a solution of this strength. This will give the percentage of manganese in the spelter. The chemical equivalent of this amount

zinc should be deducted from the percentage of zinc previously ob-
ned.

If cadmium is present, it will also remain in solution with the zinc and
ll affect the titration in a manner similar to the manganese. It is
ually present in such very small amounts that it is not readily precipi-
ed by hyrdogen sulphide except from a nearly neutral solution, in
ich part of the zinc is also precipitated. It is therefore necessary to
ke a separate determination of the cadmium and correct the apparent
ount of zinc, as was done in the case of manganese. Another alterna-
e, which has given me doubtful success in the case of such small amounts,
to boil the solution for a few minutes with a piece of aluminum foil
t previous to titration. The aluminum thus introduced into the
ution does not affect the result. Usually, however, unless specially
ted for, cadmium is always counted as zinc.

To Determine Zinc in Ores.—Decompose one gram of the sample in a
ker with hydrochloric acid, or if necessary with aqua regia. Evapo-
e to dryness, and if nitric acid has been added, re-dissolve in hydro-
oric acid and evaporate again. Dissolve in 15 cc. of hydrochloric
d (1.20), dilute with water, filter and wash. Burn off the filter (unless
contains lead) in a platinum crucible and treat with hydrofluoric and
phuric acids—exactly as in a silica determination. Dissolve the residue
hydrochloric acid and add to the solution. Usually this treatment of the
idue is not necessary, as it rarely contains more than a few hundredths
a per cent. of zinc. If lead sulphate is present in this residue, use a
forated crucible with an asbestos felt for a filter. Remove the fil-
te after washing the residue thoroughly and dissolve out the lead
phate with a strongly ammoniacal solution of ammonium citrate.
ish with hot water and then transfer the remaining residue, together
h the felt, to an ordinary platinum crucible and treat wih hydrofluoric
d as before, finally adding the hydrochloric acid solution of the re-
ining residue to the filtrate. (Advantage may be taken of the above
ps to determine the lead in the same portion—the only changes neces-
y being to evaporate with sulphuric acid instead of hydrochloric and
weigh the perforated crucible before and after treatment with the
monium citrate, calling the difference lead sulphate.) Neutralize
filtrate with ammonia and again acidify, adding about 3 cc. of acid
excess for every 200 cc. of solution. Pass hydrogen sulphide through
solution to remove the copper group and, having filtered out the pre-
itate thus obtained, heat until the free hydrogen sulphide has boiled
and then add an excess of bromine water and evaporate to about
cc. Precipitate the iron with ammonia, using a large excess and
shing with water containing ammonia. If the precipitate amounts
more than a few tenths of a per cent. it should be dissolved and re-

precipitated and in case of large amounts of iron a third precipitation is sometimes necessary. Acidify the filtrate with hydrochloric acid, adding 3 cc. in excess. The solution is now ready for titration, unless manganese is present, if its volume does not exceed 150 to 200 cc. If it is of larger bulk than this, it should be evaporated until of approximately this volume, before titration. In the case of very large amounts of iron the sulphide of zinc should be separated from it just as described below when nickel is present, or, if preferred, the ether separation may be used.

When Manganese is Present in the Ore.—If the iron is small in amount, add to the solution after evaporation, but before removing the iron, five grams or more of potassium or sodium bromide. Make strongly ammoniacal and stir for an hour by means of some such device as that used for the solution of steels in the determination of carbon. If no appliance of this sort can be had, the solution should be allowed to stand over night at room temperature. The manganese and iron are completely precipitated and should be filtered off and washed with water containing ammonia. The filtrate should then be acidified as above and titrated. If the iron is present in large enough quantities to require re-precipitation, it should be removed before treatment with the bromide; but if both the manganese and iron are precipitated together, as above, and it is desired to re-precipitate them, they should be dissolved in a mixture of hydrochloric and sulphurous acids, the solution boiled to expel the sulphurous fumes and then oxidized with bromine water. The bromine should be boiled off as before and the precipitation then repeated with the alkali bromide and ammonia. The amount of bromide may be varied without any effect on the titration. If it is desired to determine the manganese, it may be dissolved in sulphurous acid alone, and after solution is complete, nitric acid added, the nitrous fumes boiled out and the determination completed by the Bismuthate Method.

Of course the manganese may be readily avoided by precipitating the zinc as sulphide from a slightly acid solution and this is to be advised in the case of large amounts of manganese—also, if any nickel is in evidence. The presence of nickel will be made known by a blue color of the ammoniacal filtrate from the iron. If it is necessary to precipitate the sulphide of zinc to avoid these metals, the best plan is to evaporate the hydrochloric acid as first obtained to a small bulk in order to expel most of the free acid, dilute with a little water and neutralize with sodium carbonate solution, using methyl orange as an indicator. The neutral point should be carefully obtained and then *ten drops* of hydrochloric acid added. Wash down the sides of the beaker, dilute to 200 cc. and pass hydrogen sulphide through the *cold* solution for an hour. Let the solution stand for several hours, or, if convenient, over night before filtering. Zinc sulphide precipitated in this way should filter out like

so much sand. Put the paper containing the precipitate into a beaker and digest until dissolved in 10 cc. of hydrochloric acid diluted with water. Pass hydrogen sulphide for a few minutes to be sure that all the copper is precipitated and then filter and wash thoroughly with hot water. Evaporate the filtrate after adding a slight excess of bromine water to oxidize any iron that may have been occluded by the zinc, and when it is reduced to a small volume add an excess of ammonia and boil. Filter, if necessary, and neutralize the filtrate with hydrochloric acid, adding 3 cc. in excess. Dilute to 150 cc. and titrate. This method is excellent if the conditions are just right, but my idea has been to avoid a precipitation of the zinc, if possible, and thus get rid of what may be a troublesome filtration. Accordingly, I have endeavored, except in cases where nickel is present, to precipitate from the zinc all metals interfering with the titration.

Brasses.—Remove the tin, copper and lead in the usual way—by solution in nitric acid, filtration of the metastannic acid, and deposition of the two latter metals by electrolysis. If it is certain that the copper is entirely removed, evaporate to dryness the nitric acid solution, which now contains only the zinc and perhaps a small amount of iron. Dissolve the residue in 10 cc. of strong hydrochloric acid and, after dilution, precipitate the iron with ammonia, being careful to boil long enough to insure a complete precipitation, as iron comes down very slowly when present in such small quantities. Filter and wash with dilute ammonia water and then with hot water. Neutralize the filtrate with hydrochloric acid, add an excess of 3 cc., dilute to 150 cc., and titrate with the standard ferrocyanide solution. In the case of a manganese bronze, the only modification would be the treatment with alkali bromide, as described above under ores.

It is sometimes easier, in the case of brasses, to make the filtrate from the electrolysis ammoniacal and add colorless ammonium sulphide. Digest at a temperature near the boiling-point for about an hour, allow to settle and filter, keeping as much of the precipitate in the beaker as possible. When the liquid has run through the funnel, replace the filtrate beaker by the one containing the precipitate and pour dilute hydrochloric acid over the filter, allowing it to run through on to the main bulk of the precipitate. Wash the filter once or twice and heat the solution until the zinc is dissolved. Pass a current of hydrogen sulphide for a few minutes and filter out any small traces of copper that may be precipitated as sulphide. Oxidize the filtrate with bromine water and evaporate to a small volume, finally precipitating the small amount of iron and finishing as before.

Aluminum Alloys Containing Zinc.—Aluminum does not affect the ferrocyanide and so the natural idea would be to dissolve in hydrochloric

acid and proceed directly with the titration as soon as solution was complete. But iron is almost always present in such alloys to a considerable amount, and hence the necessity for a more roundabout method. Dissolve one gram in either nitric or hydrochloric acid. Add a few crystals of citric acid, make ammoniacal, and heat to boiling. Remove from the source of heat and add a little colorless ammonium sulphide. Allow to settle and then filter, being careful to wash out the last traces of citric acid with a wash water containing a little ammonium sulphide. The precipitate will consist of sulphide of zinc, iron and copper metals. Treat it exactly as described for brasses under similar conditions. If desired, the metal may be dissolved in hydrochloric acid and the zinc precipitated as sulphide from a slightly acid solution just as when it is required to separate it from nickel.

In general, any one working intelligently, realizing the final conditions and knowing something of the material in hand, will find no difficulty in following out the plan of this method.

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THE DETERMINATION OF BENZENE IN ILLUMINATING GAS.

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I. The Absorption of Benzene by Ammoniacal Nickel Nitrate.

In 1903 Dennis and O'Neill described[1] an absorption method for the determination of benzene in illuminating gas. The absorbent there recommended was an ammoniacal solution of nickel nitrate, the use of such a solution for the determination of benzene having been suggested by the statement of Hofmann and Küspert[2] that when illuminating gas acts upon a mixture of nickel hydroxide and ammonia, there is formed a compound of nickel cyanide with ammonia and benzene, $Ni(CN)_2.NH_3.C_6H_6$.

In practice, this method for the determination of benzene in some localities, has given most excellent results, while in other quarters it has been far from satisfactory. Morton recently demonstrated[3] that when mixtures of *benzene and air* are analyzed with the use of the reagent, the results are scarcely better than might be obtained with water alone, and that, moreover, the efficiency of the absorbent steadily decreases as the amount of benzene that it has taken up increases. These statements of Morton have been substantiated in this laboratory and the

[1] This Journal, 25, 503.
[2] Z. anorg. Chem., 15, 204 (1897.)
[3] This Journal, 28, 1728 (1906).

only explanation of the excellence of the results in the analyses of mixtures of air and benzene as published by Dennis and O'Neill would seem to lie in the fact that but few absorptions of benzene were made and that, consequently, the reagent had not taken up sufficient benzene to render the loss in its absorbing power noticeable.

Confronting the facts adduced by Morton, however, were arrayed statements from several University and technical laboratories testifying to the satisfactory character of the method and the uniformity of results obtained by it in analyses of illuminating gas. In seeking for explanation of these variations in the reports of different chemists it occurred to the authors of the present paper that those samples of illuminating gas on which the method gave good results might have contained cyanogen compounds necessary to the formation of the compound that Hofmann and Küspert described, while the poor results on other samples of illuminating gas might be caused by the absence of cyanogen compounds from the gas. To test the validity of this assumption, the ammoniacal nickel nitrate solution recommended by Dennis and O'Neill was used in a series of analyses of a gas mixture containing benzene, hydrocyanic acid and air.

The hydrocyanic acid gas for these analyses was prepared by filling a Hempel nitrometer with mercury, then introducing from five to ten cubic centimeters of a concentrated solution of potassium cyanide and adding gradually through the side arm about the same volume of hydrochloric acid (one part of acid to one part of water). The gas set free by this reaction was completely absorbable by caustic potash. It probably contained small amounts of cyanogen and carbon dioxide but it will be referred to below as "hydrocyanic acid." A mixture of this gas with benzene and air was obtained by measuring off a volume of air, then passing this into a Hempel simple gas pipette containing liquid benzene, drawing the gas back into the burette and noting the increase in volume, and finally drawing into the burette the hydrocyanic acid gas that had been evolved in the nitrometer, and again measuring the volume. The measurements were made in a jacketed Hempel gas burette with mercury as the confining liquid. Several mixtures prepared in this manner were analyzed by the Dennis and O'Neill method. The same sample of ammoniacal nickel nitrate was employed for all of the absorptions listed in Tables I, II and III.

Table I gives the results obtained with the mixture of air, benzene and hydrocyanic acid. The completeness of the absorption may be seen by comparing the volume of air taken with the volume of gas remaining after absorption. It will be noted that the agreement is practically exact in every case except the 4th.

TABLE I.

Number of experiment.	Air taken. cc.	Benzene taken. cc.	Hydrocyanic acid gas taken. cc.	Volume remaining after absorption by ammoniacal nickel nitrate. cc.
1	56.2	1.0	3.2	56.2
2	56.4	0.6	2.4	56.5
3	56.5	1.9	2.4	56.5
4	56.8	3.4	5.5	57.1
5	57.7	1.5	1.2	57.7
6	58.1	1.4	1.5	58.1
7	58.2	2.1	6.1	58.3
8	59.1	0.8	1.3	59.1

While the above table demonstrates that, in the presence of cyanogen compounds, ammoniacal nickel nitrate quantitatively absorbs benzene vapor, the accurate results obtained by some analysts with the reagent could even yet not be explained, if these cyanogen compounds in a gas mixture are completely removed by potassium hydroxide, the reagent that precedes the ammoniacal nickel nitrate in the analysis of illuminating gas. To ascertain whether any of the cyanogen compounds are left in the gas mixture after it has been passed into the potassium hydroxide pipette, the analyses given in Table II were made. In each analysis the gas mixture was allowed to remain in the potassium hydroxide pipette for such a length of time as had been found to suffice for the absorption of all of the hydrocyanic acid when that was mixed with air alone. The results show that when hydrocyanic acid, benzene and air are present together, potassium hydroxide does not remove all of the hydrocyanic acid, the benzene appearing to exert a deterrent effect upon the absorption. It will be noted that the ammoniacal nickel nitrate quantitatively removed the benzene and the residual hydrocyanic acid in nearly every case.

TABLE II.

Number of experiment.	Air taken. cc.	Benzene taken. cc.	Hydrocyanic acid gas taken. cc.	Volume absorbed by potassium hydroxide. cc.	Volume absorbed by ammoniacal nickel nitrate. cc.	Volume remaining after absorption by ammoniacal nickel nitrate. cc.
9	59.4	1.4	7.2	6.9	1.7	59.4
10	59.9	0.5	8.6	8.4	0.5	60.1
11	60.2	1.1	3.1	3.0	1.1	60.3
12	56.1	0.9	5.5	4.8	1.6	56.1
13	56.4	0.9	1.7	1.6	1.0	56.4
14	56.7	1.3	2.0	1.8	1.5	56.7
15	57.0	0.7	14.3	13.1	1.8	57.1
16	57.8	1.7	1.9	1.9	1.7	57.8

If, from the results in the above table, we are justified in assuming that after treatment with caustic potash some cyanogen compounds still remain in illuminating gas, it at once becomes evident why the

Dennis and O'Neill method gave satisfactory results with such samples of illuminating gas as contained cyanogen compounds.

After the first three determinations in Table II had been made, it was thought possible that the ammoniacal nickel nitrate had then taken up sufficient hydrocyanic acid to enable it to absorb benzene vapor without the addition of further hydrocyanic acid gas to the mixture. This assumption seems also to be borne out by the fact that in Determinations 11 and 13 the absorption of benzene was complete even when only 1/10 of a cubic centimeter of "hydrocyanic acid" gas was present with the benzene vapor. The results of these analyses are given in Table III.

TABLE III.

Number of experiment.	Air taken. cc.	Benzene taken. cc.	Volume absorbed by ammoniacal nickel nitrate. cc.
17	60.5	1.5	1.5
18	60.5	1.9	1.8
19	60.9	0.9	0.7
20	60.8	1.4	1.4
21	61.2	0.7	0.7

The results, Nos. 12 to 21 inclusive, demonstrate that after the ammoniacal nickel nitrate has taken up some cyanogen it is able quantitatively to absorb fairly large amounts of benzene vapor, and that if cyanogen compounds are present in illuminating gas, the benzene content may accurately be determined by the method of Dennis and O'Neill. If, however, the reagent contains no cyanogen compounds and if none are present in the gas that is being analyzed the method will not give accurate results.

II. The Absorption of Benzene by Ammoniacal Nickel Cyanide.

The foregoing experiments having demonstrated that a solution of ammoniacal nickel nitrate cannot be relied upon for the absorption of benzene from all samples of illuminating gas, the necessity arose for such modification of the method as would render it uniformly accurate.

It is apparent that to insure complete absorption of the benzene from all gas mixtures through the formation of the ammonia benzene nickel cyanide, cyanogen must be present in every case. This led to the use of an ammoniacal solution of nickel cyanide[1] as an absorbent in place of the ammoniacal solution of nickel nitrate.

Preparation of the Ammoniacal Solution of Nickel Cyanide.—To 50 grams of nickel sulphate ($NiSO_4.7H_2O$), dissolved in 75 cc. of water, are added 25 grams of potassium cyanide dissolved in 40 cc. of water. After the addition of 125 cc. of ammonium hydroxide (Sp. Gr. 0.91) the mixture is shaken until the nickel cyanide has completely dissolved and is then

[1] See also Hofmann and Arnoldi, Ber., 39, 339 (1906).

allowed to stand at a temperature of 0° for twenty minutes. The clear liquid is decanted from the crystals of potassium sulphate that have been precipitated, and is treated with a solution prepared by dissolving 18 grams of crystallized citric acid in 10 cc. of water. After the mixture has stood again at 0° for ten minutes, the greenish blue supernatant solution is decanted and is introduced into a gas pipette. Two drops of liquid benzene are now added to the reagent through the large tube of the pipette and the pipette is shaken until the benzene has combined with the reagent. This is effected in two or three minutes. This addition of benzene to the reagent is made because it was found that at times a freshly prepared solution of the ammoniacal nickel cyanide did not quantitatively remove benzene vapor until it had been used for four or five determinations and had absorbed some of the substance. Hofmann and Arnoldi used acetic acid in the preparation of the absorbent. This we have replaced by citric acid because of the appreciable vapor tension of acetic acid at ordinary temperatures.

Apparatus Employed.—The reagent was placed in a Hempel gas pipette of the form used for the absorption of heavy hydrocarbons by means of fuming sulphuric acid, the upper bulb that is filled with broken glass being, however, 4.6 cm. in diameter which is somewhat larger than in the usual Hempel pipette. The measurements of the gas volumes were made in a Hempel gas burette provided with a water jacket and if changes of temperatures occurred, corrections were made for them. Numerous experiments showed that satisfactory results may be obtained with either water or mercury as the confining liquid in the burette.

Analytical Procedure.—After the sample of gas has been measured in the burette, the burette is connected by means of the usual capillary tube with a pipette containing the ammoniacal nickel cyanide solution, and the gas mixture is repeatedly passed over into the pipette and drawn back into the burette for a period of about two minutes. The pipette is then disconnected and the gas is passed into a "fuming sulphuric acid" Hempel gas pipette containing a five per cent. solution of sulphuric acid, this being done to remove the ammonia that enters the gas mixture from the reagent. The ammonia is not easily absorbed by the dilute sulphuric acid and the gas mixture must, consequently, be passed into and withdrawn from the pipette repeatedly for about two minutes to effect its complete removal.

Experimental Results.—The experiments that were made to ascertain the applicability of the reagent to the absorption of benzene and the accuracy of the method may be classified under the following heads:

(1) Determination of Benzene in Known Mixtures of Benzene and Air;

(2) Study of the Behavior of an Ammoniacal Solution of Nickel Cyanide toward Known Mixtures of Ethylene and Air;

(3) The Determination of Benzene in Coal Gas;

(4) The Determination of the "Analytical Absorbing Power" of the Ammoniacal Solution of Nickel Cyanide;

(5) The Determination of Benzene in Coal Gas that Had Been Freed from the Benzene that it Originally Contained and Had Been Mixed with Known Volumes of Benzene Vapor; and

(6) The Determination of the Vapor Tension (with Reference to Benzene) of the Partially Exhausted Reagent.

(1) *The Determination of Benzene in Known Mixtures of Benzene and Air.*—Air was drawn into the gas burette and measured. It was next passed into a gas pipette containing mercury and a few cubic centimeters of liquid benzene, and was then drawn back into the burette and the increase in volume was noted. The percentage of benzene was then determined by absorption with the ammoniacal solution of nickel cyanide with the subsequent removal of the ammonia by dilute sulphuric acid in the manner described above. A large number of these analyses was made. The few results in Table IV illustrate the average efficiency of the method.

TABLE IV.

Number of experiment.	Benzene taken. Per cent.	Benzene found. Per cent.	Number of experiment.	Benzene taken. Per cent.	Benzene found. Per cent.
22	2.3	2.3	28	1.6	1.6
23	2.6	2.6	29	1.8	1.8
24	1.2	1.3	30	1.8	1.7
25	4.9	4.9	31	5.2	5.1
26	5.1	5.1	32	2.7	2.7
27	2.7	2.7			

(2) *A Study of the Behavior of an Ammoniacal Solution of Nickel Cyanide towards Known Mixtures of Ethylene and Air.*—Ethylene was prepared by reducing an alcoholic solution of pure ethylene bromide with a zinc-copper couple. The ethylene employed in the first experiments was made in a flask and the resulting gas was found to contain about 90 per cent. of ethylene. In later experiments the preparation was carried on in a Hempel nitrometer, and the resulting ethylene was then found to be completely absorbable by 20 per cent. fuming sulphuric acid. Mixtures of ethylene and air were prepared and passed over into the ammoniacal nickel cyanide. In no case was any absorption of ethylene noted after the reagent had been shaken once with the gas mixture and thus saturated with it. The data of two experiments are given as illustrative of the results here obtained: Per cent. of ethylene taken 4.3, found 0.0; again, ethylene taken 10.4, found 0.0.

(3) *The Determination of Benzene in Coal Gas.*—A large number of determinations of the benzene naturally occurring in coal gas was made by the above method and the results are given in Table V. It is perhaps unnecessary to state that here, as in all other absorption methods in gas analysis, freshly prepared reagents should first be shaken with the sample of the gas to be analyzed in order to saturate the reagent with the slightly soluble constituents of the gas mixture. Moreover, the same sample of reagent should not be used for the analysis of gas mixtures of markedly different compositions.

TABLE V.

Number of experiments	Date.	Time of contact with reagent. Minutes.	Benzene found Per cent.
33	Jan. 7	4	0.8
34	Jan. 7	2	0.8
35	Jan. 7	2	0.8
		4 more	0.8
36	Feb. 13	2	0.7
37	Feb. 13	2	0.7
38	Feb. 13	4	0.7
39	Feb. 13	2	0.7
40	Feb. 15	6	0.6
41	Feb. 15	4	0.6
42	Feb. 15	2	0.6
43	Feb. 18	2	0.8
44	Feb. 18	2	0.8
		2 more	0.8
45	Feb. 18	6	0.8
46	Feb. 19	2	0.5
47	Feb. 19	2	0.5
		2 more	0.5
48	June 3	2	1.2
49	June 3	2	1.2
50	June 3	2	1.3
51	June 3	2	1.2
52	June 3	4	1.2
53	June 3	4	1.2
54	June 3	2	1.2
		2 more	1.2
		2 more	1.2

The results tabulated above demonstrate that an ammoniacal solution of nickel cyanide completely removes the benzene from coal gas in two minutes. It should be understood that the gas mixture is repeatedly passed into and drawn out of the gas pipette during this time.

(4) *The Determination of the "Analytical Absorbing Power" of the Ammoniacal Solution of Nickel Cyanide.*—The term "analytical absorbing power" was introduced by Hempel and means one-fourth of the total volume of the gas that one cubic centimeter of the reagent is able

absorb.[1] Theoretically, one cubic centimeter of the ammoniacal olution of nickel cyanide will absorb about 20 cc. of benzene vapor easured under ordinary conditions of temperature and pressure. This orresponds to an "analytical absorbing power" of 5 cc. of benzene vapor nd inasmuch as the gas pipette holds 200 cc. of the reagent, this volume ould suffice for the absorption of 1000 cc. of benzene vapor. The ompound that is formed, $Ni(CN)_2.NH_3.C_6H_6$, exhibits, according to e experiments of Hofmann, no measurable vapor tension.

To ascertain whether this theoretical "analytical absorbing power" as in accord with actual results, the reagent that had been used in xperiments 48 to 53 inclusive, was shaken with 2 cc. of liquid benzene quivalent to about 500 cc. of benzene vapor) until this was completely sorbed. This reagent was then employed in Experiment 54 and in Exriments 68 to 72 inclusive. The completeness of the absorption obined in each case shows conclusively that the limit of the absorbing ower of the reagent had not yet been reached even when one filling the pipette had taken up over 500 cc. of the benzene vapor. Further amination of the absorbing power demonstrated that even after a petteful of the reagent had absorbed 800 cc. of the benzene vapor quantative results could still be obtained. Since, however, the compound benzene with the reagent separates as a precipitate, it is advisable, order to avoid the clogging of the pipette, to filter the reagent after it has ken up fairly large amounts (from 200 to 400 cc.) of benzene vapor.

(5) *The Determination of Benzene in Known Mixtures of Coal Gas and enzene.*—These determinations were carried out to ascertain whether enzene can be determined accurately in the presence of the other gases at are usually found in coal gas. The sample of coal gas was first eed from benzene by treatment with the ammoniacal nickel cyanide nd then known amounts of benzene were added to it in the manner ove described.

In Experiments 64 to 67 inclusive, one sample of coal gas was emloyed and to this successive portions of benzene vapor were added, nd were then removed by absorption with the reagent. The fact that e volume of the gas residue remained constant throughout these analyes demonstrates that the constituents of ordinary coal gas other than enzene (with the exception of those gases absorbed by a concentrated olution of potassium hydroxide) are not absorbed by the reagent. This onclusion is corroborated by the fact that in Experiments 57, 58, and 1, a prolongation of the contact between the gas and reagent did not ause further appreciable diminution in the volume of the gas residue.

[1] See Hempel, Methods of Gas Analysis, Translated from 3rd German Editio y Dennis, page 145.

TABLE VI.

Number of experiment.	Time of contact with reagent. Minutes.	Benzene taken. Per cent.	Benzene found. Per cent.
55	2	1.1	1.1
56	2	2.8	2.8
57	4	0.8	0.7
58	8	0.8	0.8
59	2	4.3	4.3
60	2	2.7	2.7
61	12	2.7	2.8
62	2	0.9	0.9
63	2	0.7	0.7
64	2	0.9	0.9
65	2	1.1	1.1
66	2	1.3	1.4
67	2	1.3	1.3
68	2	1.4	1.4
69	2	1.2	1.2
70	2	1.0	1.0
71	2	2.6	2.7
72	2	3.6	3.6

(6) *The Determination of the Vapor Tension (with Reference to Benzene) of the Partially Exhausted Reagent.*—Although Hofmann states that the ammonia benzene nickel cyanide exhibits no appreciable vapor tension, it was still deemed desirable to ascertain whether the reagent, after somewhat extended use, would show a measurable benzene vapor tension. To this end a measured sample of air was brought into contact with a pipetteful of the reagent that had previously absorbed about 800 cc. of benzene vapor. The sample of air was then drawn back into the burette, was passed into a pipette containing dilute sulphuric acid, and was then drawn back into the burette and measured. The results were as follows:

Volume air taken (cc.)	60.7	61.4	74.8	89.2	83.1	73.9
Volume after contact with reagent (cc.)	60.7	61.3	74.8	89.3	83.1	73.9

From these experiments it appears that the benzene vapor tension of the partially exhausted reagent is so slight as to be negligible.

Dennis and O'Neill[1] determined experimentally that benzene is not taken up by the concentrated solution of potassium hydroxide that is employed in the Hempel method for the determination of carbon dioxide, and that consequently absorption of carbon dioxide may properly precede the determination of benzene. This point has been examined further by the authors of the present paper who also have found that potassium hydroxide solution does not absorb benzene from mixtures of benzene vapor and air. The order of procedure then in the analysis

[1] *Loc. cit.*, p. 507.

coal gas should be that recommended by Dennis and O'Neill,[1] the osorption of benzene being effected by the ammoniacal solution of ickel cyanide in place of the solution of ammoniacal nickel nitrate hich they there suggested.

I. The Morton Method for the Determination of Benzene in Illuminating Gas.

D. A. Morton has recently described[2] a simple method for the deterination of benzene by absorption with concentrated sulphuric acid Sp. Gr. 1.84) and before leaving this work it was thought advisable examine Morton's method with a view to ascertaining the accuracy the results that can be obtained through its use. It is self-evident at for the determination of benzene in coal gas, there must be employed absorbent that does not remove ethylene. Morton states that the fect due to the absorption of ethylene by concentrated sulphuric acid insignificant. This statement is somewhat surprising, for inasmuch both benzene and ethylene are quantitatively absorbed by fuming lphuric acid it would seem reasonable to suppose that concentrated lphuric acid would also take up ethylene, and that, although it might osorb this gas in smaller amounts than did the fuming sulphuric acid, e percentages of ethylene removed by it would yet be appreciable. urther, it was deemed possible that the apparently correct results in e separation of benzene and ethylene obtained by Morton might be cribed to an accidental balancing of errors in the removal of the two ses in question. In looking up the literature of the subject it was und that Frankland and Thorne,[3] in working upon "The Luminosity Benzol" found "that ordinary sulphuric acid absorbs benzol vapor ther rapidly, and may be used for its eudiometric determination." hey were, however, separating benzene from hydrogen, carbon monoxe, and methane, and no ethylene was present in the gas mixture that as employed. Butlerow and Gorjainow[4] found that concentrated lphuric acid will completely absorb ethylene at a temperature of from o° to 170°. Berthelot[5] states that when ethylene is shaken with ncentrated sulphuric acid, 100 grams of the acid absorb 6.7 liters 20 volumes) of ethylene, and further that the ethylene that escapes osorption upon passage through a Liebig bulb containing fuming sulruric acid is afterward absorbed by shaking it with ordinary sulphuric id. In a paper by Faraday[6] it is stated that when ethylene was al-

[1] *Loc. cit.*, p. 511.
[2] This Journal, 28, 1732 (1906).
[3] J. Chem. Soc., 33, 89 (1878).
[4] Ber., 6, 196 (1873).
[5] Ann. chim. phys. [3], 43, 385 (1855).
[6] Phil. Trans., 1825, p. 448.

lowed to stand for eighteen days in contact with concentrated sulphuric acid one volume of the acid absorbed 84.7 volumes of the ethylene.

Experimental.

The Absorption of Ethylene by Sulphuric Acid (Sp. Gr. 1.84).—Ethylene was prepared in the manner above described. A mixture of air and ethylene containing 22.5 per cent. of ethylene was made and was shaken for one minute with about 150 cc. of concentrated sulphuric acid contained in a Hempel simple gas pipette. It was then drawn back into the burette and the diminution in volume noted. It was passed back again into the pipette and shaken for another minute and measured. This was repeated several times and the results are given in Table VII. It will be noted that 18 cc. of the 22.5 of ethylene present in the gas mixture was absorbed in thirty minutes, the rate of absorption diminishing as the percentage of ethylene decreased.

TABLE VII.

Number of experiment.	Ethylene present in 100 cc. of gas mixture. cc.	Ethylene absorbed. cc.	Length of each shaking with concentrated H_2SO_4. Minutes.	Total length of contact with concentrated H_2SO_4. Minutes.	Total volume ethylene absorbed. cc.
73	22.5	2.3	1	1	2.3
74	20.2	1.9	1	2	4.2
75	18.3	1.3	1	3	5.5
76	17.0	1.3	1	4	6.8
77	15.7	1.2	1	5	8.0
78	14.5	1.2	1	6	9.2
79	13.3	0.8	1	7	10.0
80	12.5	0.8	1	8	10.8
81	11.7	1.0	1	9	11.8
82	10.7	1.0	1	10	12.8
83	9.7	0.8	1	11	13.6
84	8.9	4.4	19	30	18.0

The Action of Concentrated Sulphuric Acid upon a Mixture of Air, Ethylene and Benzene.—A mixture of air, ethylene and benzene containing 1.5 per cent. benzene and 10 per cent. ethylene was prepared and was shaken with concentrated sulphuric acid in the manner that Morton describes, except that in Analyses 89 and 91, the shaking was continued for two minutes instead of only one minute. The results are given in Table VIII. It will be seen that of a total of 11.5 cc. of hydrocarbons in 100 cc. of the gas mixture, 8.2 cc. were absorbed in nine minutes. There was but 1.5 per cent. of benzene present in the original mixture and yet 4.3 per cent. of the hydrocarbons was absorbed in the first minute of shaking with the sulphuric acid, demonstrating that at least 2.8 per cent. of ethylene was removed by the reagent. If the analyst is to regard the absorption by sulphuric acid as indicative of the per cent. of benzene present, the actual error in this case would be very

large. By further shaking of this mixture with the concentrated sulphuric acid from 0.3 per cent. to 0.7 per cent. more of the hydrocarbons was absorbed per minute.

TABLE VIII.

Number of experiment.	Hydrocarbons present in 100 cc. gas mixture. cc.	Hydrocarbons absorbed. cc.	Length of contact with concentrated H_2SO_4. Minutes.	Total length of contact with concentrated H_2SO_4. Minutes.	Total volume hydrocarbons absorbed. cc.
85	11.5	4.3	1	1	4.3
86	7.2	0.7	1	2	5.0
87	6.5	0.3	1	3	5.3
88	6.2	0.5	1	4	5.8
89	5.7	1.4	2	6	7.2
90	4.3	0.3	1	7	7.5
91	4.0	0.7	2	9	8.2

The Action of Concentrated Sulphuric Acid upon Mixtures of Air with Varying Amounts of Ethylene and Benzene.—In this series of experiments the gas mixture was first shaken for one minute with the concentrated sulphuric acid and was then passed into a pipette containing ammoniacal nickel cyanide solution to ascertain whether all of the benzene originally present had been absorbed by the sulphuric acid. An examination of the results in Table IX shows that the gas absorbed by the concentrated sulphuric acid is not benzene alone, for upon comparing the figures in the third and fourth columns it will be seen that in Experiments 96 to

TABLE IX.

Number of experiment.	Ethylene taken Per cent.	Benzene taken. Per cent.	Hydrocarbons absorbed in one minute by concentrated sulphuric acid. Per cent.	Hydrocarbons afterward absorbed by ammoniacal nickel cyanide solution. Per cent.
92	0.3	10.8	9.9	1.2
93	0.5	11.0	9.4	1.5
94	0.7	7.2	6.9	0.3
95	1.3	5.4	5.5	0.2
96	1.3	2.7	3.0	0.2
97	1.4	0 8	1.0	0.0
98	2.1	2.1	2.5	0.0
99	2.3	4.9	5.7	0.0
100	2.3	2.3	2.1	0.2
101	2.7	2.4	3.0	0.0
102	2.8	5.6	5.2	0.4
103	3.3	1.2	1.7	0.0
104	3.7	1.7	2.4	0.5
105	3.9	0.7	1.2	0.3
106	4.2	0.7	1.2	0.1
107	5.2	1.9	2.0	...
108	5.2	0.9	1.3	...
109	6.3	0.7	1.0	0.2
110	12.6	2.9	3.3	...
111	15.8	3.0	4.1	...

111, with the exception of the 100th and 102nd, the volume of gas absorbed is greater than the volume of benzene taken, in many cases considerably greater. Moreover, the absorption of the benzene by the concentrated sulphuric acid is frequently incomplete, as is demonstrated by the results in the last column. In some cases the measurements showed that the volume of gas absorbed by the sulphuric acid is greater than the volume of benzene added, and yet even in these cases not all of the benzene that had been added was removed by the sulphuric acid. (See in particular, Experiments 96, 104, and 105). The results in Table IX would further demonstrate that with so large and so irregular variations a correction factor for the absorption of ethylene as suggested by Morton would be of no value.

The Determination of Benzene in Coal Gas by means of Concentrated Sulphuric Acid.—A series of determinations (Table X) of benzene in coal gas was made by the Morton method. At the time when these analyses were made the coal gas showed by the ammoniacal nickel cyanide method an average content of less than one per cent. of benzene. The results by the Morton method are in every case much too high and furnish further proof that concentrated sulphuric acid removes other constituents than benzene.

TABLE X.

Number of experiment.	Date.	Length of contact with concentrated sulphuric acid. Minutes.	Hydrocarbons absorbed. Per cent.
112	Feb. 14	1	2.0
113	Feb. 14	1	1.9
114	Feb. 14	2	2.2
115	Feb. 14	4	2.8
116	Feb. 15	1	1.7
117	Feb. 15	1	1.9
118	Feb. 15	1	1.8
119	Feb. 15	2	2.1
120	Feb. 15	4	2.3

The Effect in the Morton Method of Varying the Speed of Shaking.—Morton directs that the gas be passed into the pipette containing the concentrated sulphuric acid and be shaken *vigorously* (twice per second) with this reagent for one minute. The experiments in Table XI were made to ascertain whether the amount of absorption by the sulphuric acid would vary if the speed at which the pipette is shaken is varied. With acceleration of the shaking slightly higher results were obtained, but they can not be taken as conclusive upon the point at issue, because the concentrated sulphuric acid when shaken foams to so great an extent as to render it difficult to obtain correct measurements of the residual gas volume. Moreover, minute gas bubbles become suspended

through the sulphuric acid and do not all of them rise to the surface of the reagent even after that has stood undisturbed for two minutes.

TABLE XI.

Number of experiment.	Length of contact with reagent. Minutes.	Number of shakes per second.	Hydrocarbons absorbed. Per cent.
121	1	1	1.9
122	1	1	1.8
123	1	2	1.8
124	1	2	2.0
125	1	4	2.2
126	1	4	2.3

To avoid the difficulty that results from the foaming of the reagent, due to shaking, the concentrated sulphuric acid was placed in a pipette of the type used for fuming sulphuric acid.[1] In the first determination the sample of coal gas was measured in the burette and was then passed into a pipette and drawn back and measured. In the second determination a fresh sample of the gas was taken and was passed into and drawn out from the pipette twice. In the next determination another sample was run into the pipette three times, and so on. The coal gas used in Experiments 127 to 134 inclusive, was found to contain by the ammoniacal nickel cyanide method 0.8 per cent. benzene. The sample of gas on the following day, February 19th, Experiments 135 to 141 inclusive, contained 0.5 per cent. benzene.

TABLE XII.

Number of experiment.	Date.	Number of times gas mixture passed into pipette.	Hydrocarbons absorbed. Per cent.
127	Feb. 18	1	1.1
128	Feb. 18	2	1.2
129	Feb. 18	3	1.4
130	Feb. 18	3	1.0
131	Feb. 18	3	1.6
132	Feb. 18	4	1.5
133	Feb. 18	6	1.6
134	Feb. 18	10	2.0
135	Feb. 19	1	0.2
136	Feb. 19	2	0.4
137	Feb. 19	3	0.7
138	Feb. 19	4	1.0
139	Feb. 19	5	1.7
140	Feb. 19	8	2.0
141	Feb. 19	11	2.1

The results given in this table show wide variations in the apparent amount of benzene present and demonstrate that the method will not give accurate results even when the foaming is avoided by the use of the fuming sulphuric acid pipette.

[1] See Hempel's Gas Analysis, page 229.

Summary.

An ammoniacal solution of nickel cyanide prepared according to the directions given in this article will quantitatively absorb benzene from mixtures containing benzene and air, and from ordinary coal gas. It will not absorb measurable quantities of ethylene or of the other constituents of ordinary coal gas, with the exception of those absorbable in potassium hydroxide solution.

The method proposed by Morton for absorbing benzene by means of sulphuric acid (Sp. Gr. 1.84) does not give constant results even when the conditions are the same, and yields widely varying results when the conditions are changed. Moreover, it absorbs both ethylene and benzene, and from mixtures containing both of these gases it does not quantitatively remove the benzene but does remove an indeterminate amount of ethylene. Moreover, in the manipulation suggested by Morton, the reagent foams to such an extent as to make the accurate reading of the gas volumes well nigh impossible.

CORNELL UNIVERSITY,
November, 1907.

THE EFFECT OF COAL GAS ON THE CORROSION OF WROUGHT IRON PIPE, BURIED IN THE EARTH.[1]

BY WM. L. DUDLEY.

Received November 14, 1907.

This investigation was undertaken in connection with a study of the conditions causing the corrosion of pipe laid under the streets in the City of Nashville.

Five samples of earth were collected as representative of the various types in which the pipes are laid.

Sample No. 1 was taken from a street at the depth of the gas pipes. It was an old fill. Sample No. 2 was taken from about 4 feet from the surface on private property in the heart of the city, 50 feet from the sidewalk, and was a yellow clay. Sample No. 3 was taken from between the car tracks just under the street metal. It was a loamy clay. Sample No. 4 was a clay taken from a vacant lot in the northern part of the city. Sample No. 5 was taken from under the car tracks in the southern part of the city, and was a mixture of clay and loam.

The analyses of the samples gave the following results in percentages:

Sample.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Moisture (sample air-dried)...	15.37	15.82	14.41	13.95	14.98
Chlorine.....	0.04204	0.01501	0.0018	0.0006	0.0024
Nitrogen, as nitrates.....	0.01501	0.22523	0.006	0.003	0.0015
Nitrogen, as nitrites.....	0.00008	0.000002	trace	none	trace
Nitrogen, as ammonia.....	0.000306	0.000165	0.000011	0.000039	0.000042

[1] Read before the New York Section of the American Chemical Society.

Sample.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Albuminoid ammonia.....	0.00128	0.000052	0.00002	0.000021	0.000021
Alkali equivalent (Na_2CO_3)...	0.0382	0.0478	0.0324	0.0057	0.0318
Sulphuric anhydride (SO_3)....	0.0134	0.019	0.0448	0.0073	0.0424
Humus	2.04	3.40	2.05	1.4	2.7

Wrought iron pipes, one inch inside diameter and ten and a half inches long, were carefully cleaned and freed from all oxide by immersing in a warm ammoniacal solution of ammonium citrate for twenty minutes (or longer if necessary), brushing with a stiff brush, rinsing with distilled water, and drying rapidly.

The ammonium citrate solution is made by dissolving 40 grams of citric acid in water and neutralizing with the requisite amount of ammonium hydroxide of sp. gr. 0.896, required by the equation:

$$C_6H_8O_7.H_2O + 3NH_4OH = \text{Etc.}$$

The solution is then diluted to 460 cc. and contains approximately 10 per cent. of ammonium citrate. The citrate solution acts more rapidly on the iron oxide when warmed and has very little effect on metallic iron. A clean and bright piece of iron, having a surface of about 15 square inches, was allowed to remain in the solution for 24 hours, and no effect on the surface was observed nor was any appreciable loss of weight noted.

The pipes were weighed and plugged at one end with corks driven in about one-eighth of an inch beyond the edge, and this space was filled with melted paraffin to keep the moisture in the earth from getting inside.

The samples of earth were each put in a wooden box of one cubic foot capacity, painted inside with asphalt paint to prevent the soluble constituents of the wood from permeating the earth. The pipes were placed in an upright position in the boxes (with the closed ends down) and the samples of earth were carefully tamped around them to within one inch of the top.

The earth in each box was to have been sprinkled daily with 50 cc. of water, so as to maintain natural underground conditions as far as possible, but the person in charge of this series of experiments neglected this precaution during a large part of the time. However, as each received the same treatment, the results are comparable, although they are all too low, except in the case of sample No. 5, which will be referred to later.

At the end of twelve months the pipes were removed, cleaned with the citrate solution, as previously described, and weighed.

The results are as follows:

Sample of earth.	Original weight of pipe. Grams.	Final weight of pipe. Grams.	Loss of weight. Grams.
No. 1	624.49	603 93	20.56
" 2	652.45	638.92	13.53
" 3	665.76	663.20	2.56
" 4	680.81	678.30	2.51
" 5	618.90	606.50	12.40

The results, except that for sample No. 5, show that the amount of corrosion is determined practically by the chlorine content in the earth. There is some error in the result obtained from sample No. 5 which I am not able to discover, but that the result is entirely abnormal will be shown clearly later on.

The series of experiments designed to show the effects of coal gas on the corrosion of the pipe was conducted under the specified conditions in every detail. Into each box was placed an L, made of one-half inch gas pipe, one limb passing vertically down one corner of the box and the other along the bottom to the diagonal corner. The limb along the bottom was perforated on the under side with numerous one-eighth inch holes uniformly distributed and the end was plugged. The gas was admitted to this pipe through a standard meter reading to one-hundredth of a cubic foot.

One-half of a cubic foot of coal gas was admitted into each box daily, except Sundays, and at the same time the earth was moistened by sprinkling with 50 cc. of water. The boxes were covered with canvas so as to prevent the moisture from evaporating too rapidly.

In the samples of earth Nos. 2, 3, 4 and 5, two pipes were placed and the amount of corrosion of each pair shows very good agreement. The results, after twelve months, are as follows:

Sample. of earth.	Original weight of pipe. Grams.	Final weight of pipe. Grams.	Loss of weight. Grams.	Average loss of weight. Grams.
No. 1	661.53	652.36	9.17	9.17
" 2	658.30	651.77	6.53	6.34
	654.07	647.92	6.15	
" 3	663.60	662.45	1.25	1.54
	668.71	666.88	1.83	
" 4	665.62	664.37	1.25	1.17
	671.45	670.36	1.09	
" 5	653.58	651.78	1.80	1.96
	663.14	661.02	2.12	

The following table shows the comparative amount of corrosion of the pipe in the earth alone and in the earth saturated with coal gas:

Sample of earth.	Loss of weight in earth alone. Grams.	Loss of weight in earth saturated with gas. Grams.
No. 1	20.56	9.17
" 2	13.53	6.34
" 3	2.56	1.54
" 4	2.51	1.17
" 5	(12.40)	1.96

The effect of the gas in retarding corrosion of wrought iron pipe is very marked, especially when we consider that the results showing the corrosion in the earth alone are all low (except No. 5, which is manifestly

wrong) because of the failure to maintain the proper amount of moisture in the earths throughout the whole period of the test.

Per Cent of Chlorine in Earth.

The accompanying chart shows the curves, indicating the relationship between the amount of corrosion and the chlorine content; also the error in No. 5. In the series of experiments with the coal gas, Sample No. 5 shows the normal amount of corrosion. In the series with the earth alone, No. 5 should have shown about 3 instead of 12.40 grams of corrosion. My opinion is that No. 5 was inadvertently subjected to electrolysis, as the appearance of the pipe indicated it and electrolytic experiments were being carried on at the same time.

No. 2 shows a rather high corrosive power in both series of experiments, which is doubtless due to the abnormally high content of nitrogen as nitrates in this sample of earth. It is said that the location from which Sample No. 2 was taken was formerly the site of a livery stable, which would account for the high percentage of nitrates.

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[CONTRIBUTION FROM THE WELLCOME CHEMICAL RESEARCH LABORATORIES, LONDON.]

CHEMICAL EXAMINATION OF MICROMERIA CHAMISSONIS.

(*Yerba Buena.*)[1]

BY FREDERICK B. POWER AND ARTHUR H. SALWAY.

Received November 20, 1907.

The labiate plant *Micromeria Chamissonis* (Benth.) Greene (syn. *M. Douglassi* Benth.), commonly known as "Yerba Buena," is a perennial, trailing or creeping, sweet-scented herb, which is indigenous to the Pacific coast of the United States. The generic name is stated to be derived from the Greek *mikros*, small, and *meros*, part, on account of the small size of the flowers (compare Jepson's "Flora of Western Middle California," p. 463). A description of the anatomical characters of the plant, with illustrations, has been given by J. Moeller.[2]

The above-mentioned species of *Micromeria* is used to some extent medicinally, but, so far as known to us, it has never been the subject of chemical investigation, and we have therefore availed ourselves of the opportunity of making a complete examination of its constituents.

Experimental.

The material employed in this investigation consisted of a bale of the entire, air-dried herb, which was kindly placed at our disposal by Messrs. Burroughs, Wellcome & Co., of London. The genuineness of the material was assured by the fact that it had been specially collected for them in California under the supervision of a competent botanist, Mr. P. E. F. Perrédès, B.Sc., F.L.S.

Distillation of the Plant with Steam. Characters of the Essential Oil.

A quantity ($56^1/_4$ pounds $= 25^1/_2$ kg.) of the herb was submitted to steam distillation by Messrs. Stafford Allen & Sons, of London, and our thanks are due to them for having kindly conducted this operation for us. The amount of essential oil obtained was 42.3 grams, corresponding to 0.16 per cent. of the weight of air-dried plant. Towards the end of the distillation a small quantity (8.5 grams) of a semi-solid substance separated in the condenser and receiver. This was separately collected and examined.

The essential oil had a pale yellowish brown color and an agreeably aromatic, somewhat mint-like odor. Its density was 0.9244 at 20°, and its optical rotation —22° 48′ in a 1 dcm. tube. It was not completely soluble in ten times its volume of 70 per cent. alcohol, and gave no coloration with ferric chloride.

The above-mentioned, semi-solid substance was spread on a porous plate, when the oily constituent was absorbed, and a white, crystalline

[1] Read before the New York Section of the American Chemical Society, Nov. 8, 1907.

[2] Am. J. Pharm., 1882, 54, 461, from Pharm. Centralhalle, 1882, No. 29.

solid remained. This was crystallized from acetic acid, from which it separated in pearly leaflets, melting at 61.5°. It was analyzed with the following result:

0.0914 gave 0.2506 CO_2 and 0.1073 H_2O. C = 74.8; H = 13.0.

$C_{16}H_{32}O_2$ requires C = 75.0; H = 12.5 per cent.

This solid substance was thus identified as palmitic acid.

Examination of the Alcoholic Extract of the Plant.

For the purpose of a complete examination of the constituents of the plant, 36 pounds ($16^1/_2$ kg.) of air-dried material were extracted by continuous percolation with hot alcohol. After the removal of the greater portion of the alcohol, a dark green, thick extract was obtained, which weighed 4170 grams. Of this extract, 3.5 kg. were mixed with water, and the mixture distilled with steam until all the volatile substances present had been removed.

Volatile Constituents of the Alcoholic Extract.

The distillate obtained, as above described, had a distinctly acid reaction and contained a quantity of essential oil floating on the surface. It was extracted twice with ether, after which the ethereal liquid was washed with a little water, dried with anhydrous sodium sulphate, and the ether removed. About 20 grams of a pale yellowish brown essential oil, possessing an aromatic, mint-like odor, were thus obtained. When distilled under a pressure of 25 mm. it passed over between 80° and 160°, but the greater portion boiled between 120° and 140°. The oil had a density of 0.9450 at 20°, and an optical rotation of —26° 44′ in a 1 dcm. tube. It was readily soluble in 70 per cent. alcohol, thus differing from the essential oil distilled directly from the dried plant.

The acids contained in the aqueous distillate from which the essential oil had been removed were neutralized with baryta, and the liquid concentrated. About 3 grams of a barium salt were thus obtained in the form of a thick syrup, which afforded reactions indicating the presence in the distillate of formic, acetic, and butyric acids, the latter being relatively small in amount.

Non-volatile Constituents of the Alcoholic Extract.

After the removal of the essential oil and volatile acids by distillation with steam, as above described, there remained in the distilling vessel a reddish-brown, aqueous liquid (*A*) together with a large quantity of a dark green, soft resin (*B*). The resin was separated by filtration from the liquid, while still hot, and washed well with hot water, the washings being added to the filtrate.

Examination of the Aqueous Liquid (*A*).

The aqueous liquid, which was of a reddish brown color, and pos-

sessed a slightly bitter taste, was concentrated to a convenient bulk by heating under diminished pressure in a bath of hot water.

Isolation of a New Phenolic Substance, Xanthomicrol, $C_{15}H_{10}O_4(OH)_2$.

The concentrated aqueous liquid was extracted repeatedly with ether, and the several portions finally mixed. This ethereal liquid was washed with a little water, and then extracted with small successive portions of a saturated solution of sodium carbonate. The first few extractions with alkali afforded opaque liquids containing small amounts of a dark green, semi-solid sodium compound of a resinous nature, but neither from this nor from the products which separated on acidifying these liquids could anything crystalline be obtained. The alkaline liquids obtained by the subsequent extractions were, on the other hand, of an orange-yellow color, and, when acidified, yielded orange-yellow precipitates, which were collected, washed with water, and crystallized from alcohol. A substance was thus obtained in the form of fine, lemon-yellow, silky needles, melting at 225°, which was analyzed with the following result:

0.1114 gave 0.2535 CO_2 and 0.0453 H_2O. C=62.1; H=4.5.

After another crystallization the melting point of the substance remained unchanged, and it was again analyzed:

0.1099 gave 0.2522 CO_2 and 0.0450 H_2O. C=62.6; H=4.5.

$C_{15}H_{12}O_6$ requires C=62.5; H=4.2 per cent.

The only known compound of the empirical formula $C_{15}H_{12}O_6$, which has properties similar to those of the above substance, is the so-called "datiscetin," a hydrolytic product of datiscin (compare Beilstein's *Handbuch der org. Chemie*, Bd. III., p. 580). Datiscetin, however, is stated to melt at 237°, and its solution in sulphuric acid, which has a yellow color, shows a blue fluorescence. Although the above-described substance (m. p. 225°) also dissolves in concentrated sulphuric acid with a yellow color, its solution shows no fluorescence. It thus appears not to be identical with any substance hitherto recorded, and it is therefore proposed to designate it *xanthomicrol*, with reference to its yellow color, its phenolic properties, and the generic name of the plant from which it has been obtained.[1]

Xanthomicrol is readily soluble in alcohol, ethyl acetate, and acetone, and moderately soluble in ether, but only sparingly so in chloroform and benzene. It is practically insoluble in cold, but slightly soluble in hot water. It dissolves readily in cold aqueous alkalis, forming solu-

[1] According to the recent investigations of Korczyński and Marchlewski (*Chem. Centralb.*, 1906, II., 1265 and 1907, II., 700) the substance designated as datiscetin, when purified, possesses the empirical formula $C_{15}H_{10}O_6$, melts at 268–269°, and contains four hydroxyl groups. It would thus be essentially different in its composition and character from xanthomicrol.

ons which are yellow when dilute and orange-red when concentrated. is, however, not acid towards litmus, and the sodium compound, proiced by shaking an ethereal solution of the substance with the theotical quantity of sodium ethoxide, is readily decomposed on exposure the atmospheric moisture and carbon dioxide. The property which is substance possesses of combining with alkalis is therefore to be atibuted to the presence of one or more phenolic groups.

Di-acetylxanthomicrol, $C_{15}H_{10}O_6(CO.CH_3)_2$.—A small quantity of xanthoicrol was boiled for a short time with acetic anhydride, the greater part the latter removed by distillation, and the residue poured into water. he product of the reaction, which soon solidified, was collected, washed, id dried. It was then crystallized from ethyl acetate, from which it parated in pale yellow needles, melting at 116.°

The number of acetyl groups in this compound was determined by ydrolyzing weighed portions of the substance with a solution of sodium ydroxide, subsequently acidifying with sulphuric acid, and distilling ntil acid ceased to pass over.

(I) 0.1763 gave an amount of acetic acid equivalent to 9.4 cc. N/10 aOH.

(II) 0.1789 gave an amount of acetic acid equivalent to 9.7 cc. N/10 aOH.

(I) $CH_3.CO = 22.9$; (II) $CH_3.CO = 23.3$.

$C_{15}H_{10}O_6(CO.CH_3)_2$ requires $CH_3.CO = 23.1$ per cent.

Di-acetylxanthomicrol is extremely soluble in most of the usual organic lvents, but insoluble in water. It is immediately hydrolyzed by alka-, with the reproduction of xanthomicrol, $C_{15}H_{12}O_5$, melting at 225°.

The ethereal liquid from which the above-described new phenolic subance had been obtained, and from which nothing further was extracted shaking with a solution of sodium carbonate, was washed with a little ater, dried with calcium chloride, and the ether removed, when only a ry small amount of an uncrystallizable resin remained.

The aqueous liquid (*A*) which had been extracted with ether, as above scribed, was found to give a deep yellow precipitate with basic lead etate. A slight excess of the latter was therefore added, the precipite collected, washed, suspended in water, and decomposed with hydron sulphide. On filtering the mixture an orange-red liquid was obtained, nich gave a greenish black color with ferric chloride, thus indicating e presence of tannin, but nothing of a crystalline nature could be olated from it.

The filtrate from the basic lead acetate precipitate was treated with drogen sulphide for the removal of the lead, and filtered. A portion this liquid, when treated with phenylhydrazine acetate, readily elded a crystalline osazone melting at 217°, and it therefore evidently

contained a considerable quantity of glucose. The remainder of the filtrate was concentrated to a small bulk under diminished pressure, when a thick, dark-colored syrup was obtained, from which nothing of a crystalline nature separated, even after standing for several months.

Examination of the Resins (B).

The resin which had been separated from the aqueous liquid, in the manner previously described, was dried at 100°, and then weighed 480 grams, corresponding to 3.5 per cent. of the weight of air-dried plant. This resin was intimately mixed with purified sawdust, the mixture thoroughly dried, and then extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

I.	Petroleum (b. p. 40–60°)	extracted	177.12 grams	=	36.9	per cent.
II.	Ether	"	178.08 "	=	37.1	"
III.	Chloroform	"	24.00 "	=	5.0	"
IV.	Ethyl acetate	"	10.56 "	=	2.2	"
V.	Alcohol	"	48.00 "	=	10.0	"
		Total	437.76 grams	=	91.2	per cent.

I. *Petroleum Extract of the Resins.*

This was a soft solid, of a dark greenish color. It was boiled for two hours in alcoholic solution with 40 grams of potassium hydroxide, when a small quantity of ammonia was evolved. After this treatment the greater portion of the alcohol was removed, water added, and the alkaline liquid repeatedly extracted with ether. The ethereal extract, which was of an orange-red color, was washed with a little water, dried with calcium chloride, and the ether removed, when an orange-colored, semi-solid residue was obtained. This was distilled under diminished pressure, (25 mm.), in order to remove a small quantity of resinous matter, when it passed over between 240° and 350°. The distilled product was highly fluorescent, both in the fused state and in solution, and, on cooling, it solidified to a wax-like solid. On fractionally crystallizing the latter from ethyl acetate, it was found that the greater portion consisted of a compound which separated in small, glistening, pearly leaflets, and, after a few crystallizations, was obtained in a pure state. It then melted at 66–7°, and was analyzed:

0.1420 gave 0.4434 CO_2 and 0.1822 H_2O. C = 85.2; H = 14.3.

$C_{31}H_{64}$ requires C = 85.3; H = 14.7 per cent.

This crystalline substance was thus identified as hentriacontane.

The mother liquors from the crystallization of the hentriacontane yielded a further small quantity of a hydrocarbon, which, after repeated fractionation, melted at 71–4°, and probably consisted of pentatriacontane. The more readily soluble fraction that was finally deposited

consisted of a mixture of hentriacontane with a substance which crystallized in large, thin plates. The latter substance was mechanically separated and recrystallized from a mixture of ethyl acetate and alcohol, when it was obtained in the form of pearly leaflets, melting at 135°. This compound, when dissolved in chloroform, gave, with a little acetic anhydride and a drop of sulphuric acid, the color reaction characteristic of the phytosterols.

0.1590 of the air-dried substance, heated to 105°, lost 0.0074 H_2O. $H_2O = 4.7$.

0.1480 of anhydrous substance gave 0.4536 CO_2 and 0.1622 H_2O. $C = 83.6$; $H = 12.2$.

$C_{27}H_{46}O$, H_2O requires $H_2O = 4.5$ per cent.

$C_{27}H_{46}O$ requires $C = 83.9$; $H = 11.9$ per cent.

The ultimate mother-liquors, from which the above-mentioned hydrocarbons and phytosterol had been isolated, were collected and the solvent removed. A considerable quantity of a thick yellow oil was thus obtained, which was distilled under diminished pressure, and the product collected in two fractions. The fraction of higher boiling-point solidified on cooling, and a further quantity of phytosterol was isolated from it, whereas that of lower boiling-point consisted of a thick, gummy substance, having an unpleasant odor.

The alkaline, aqueous liquid, from which the above-mentioned neutral substances had been extracted by ether, contained an insoluble potassium salt, which was collected on a filter and separately examined. The salt was boiled with alcoholic sulphuric acid, in which it was soluble, and the liberated acid precipitated by the addition of water. The acid, after being collected and washed, was crystallized from alcohol, but, as it separated in a somewhat indefinite form, it was distilled under diminished pressure and then crystallized from ethyl acetate. It was thus obtained in the form of small, glistening plates, which, after a few recrystallizations, melted constantly at 80–2°.

0.0714 gave 0.2034 CO_2 and 0.0830 H_2O. $C = 77.7$; $H = 12.9$.

$C_{22}H_{44}O_2$ requires $C = 77.6$; $H = 12.9$ per cent.

This substance was evidently behenic acid. The mother-liquors from the crystallization of the latter gave deposits melting below 70°, but these were too small in amount to permit of further purification.

The alkaline liquid, from which the above-described potassium salt had been removed, was acidified with sulphuric acid and distilled with steam. The distillate contained a very small amount of volatile acid which, after conversion into a barium salt, afforded reactions indicating it to consist chiefly of butyric acid, with traces of formic and acetic acids. The contents of the distilling flask were subsequently extracted with ether, the ethereal solution being washed, dried, and the ether removed,

when a quantity (88 grams) of a dark green, soft solid was obtained. This evidently contained a considerable amount of resinous matter, which was separated by washing with light petroleum, in which the resin was insoluble. The petroleum washings, after the removal of the solvent, yielded a quantity (46 grams) of a green, wax-like solid, which was distilled under diminished pressure. The larger portion (37 grams) passed over between 230° and 250° at 20 mm., while about 3 grams were collected above 250°. Both fractions, on cooling, solidified to a wax-like mass. The larger portion was fractionally crystallized from alcohol, when from the least soluble fractions a substance was finally isolated which melted at 71–3°, and this melting-point was not altered by further crystallization.

0.0780 gave 0.2193 CO_2 and 0.0905 H_2O. C = 76.7; H = 12.9.

$C_{20}H_{40}O_2$ requires C = 76.9; H = 12.8 per cent.

This substance was thus identified as arachidic acid.

The mother-liquors, which still contained a large proportion of the fatty acids present in the mixture, gave deposits from which, by long-continued fractionation, a substance was obtained which melted quite constantly at 55–7°, and this was analyzed.

0.1522 gave 0.4182 CO_2 and 0.1740 H_2O. C = 74.9; H = 12.7.

$C_{16}H_{32}O_2$ requires C = 75.0; H = 12.5 per cent.

It is evident that this substance was nearly pure palmitic acid.

From the portion of mixed fatty acids distilling above 250°/20 mm. a very small amount of a substance was isolated which melted at 77–8°. This apparently consisted of slightly impure behenic acid, which, as already noted, had been isolated from the insoluble potassium salt formed in the hydrolysis of the petroleum extract. The mother-liquors from the above-described compounds did not decolorize bromine, and no unsaturated acids were therefore present in the original mixture.

II. *Ether Extract of the Resins.*

This was obtained in the form of a light green powder and amounted to 178 grams. It was digested with a large volume of ether, which dissolved about one-half of the total amount of extract. The sparingly soluble portion was separated by filtration from the ethereal solution, washed with a little ether, and the two portions independently investigated.

Isolation of a New Crystalline Alcohol, Micromerol, $C_{33}H_{51}O_3$–$OH,2H_2O$.

The portion of the ether extract of the resins which remained undissolved by the above treatment was dissolved in alcohol, in which it was only moderately soluble, and the solution heated with animal charcoal under a reflux condenser for several hours. By this means the dark green color of the liquid was completely removed. After filtering the solu-

ı it began to deposit a quantity of a crystalline substance in the form fine, colorless needles. The crystals were always accompanied by a ıtively small amount of amorphous, fluffy matter, but it was found t this could be removed by filtration through fine muslin, which re- ıed the crystalline substance while the amorphous matter was carried ough the filter with the mother-liquor. By repeating this operation crystalline substance was obtained in a pure condition, and further ıntities of it were deposited on concentrating the mother-liquors. : compound, when rapidly heated, melts at 277°. An analysis of it 'e the following results:

.9268 of air-dried substance, when heated for 2 hours at 105°, lost 567 H_2O. $H_2O = 7.2$.

I) 0.1291 of anhydrous substance gave 0.3652 CO_2 and 0.1201 H_2O.

II) 0.1338 of anhydrous substance gave 0.3934 CO_2 and 0.1276 H_2O.

I) C = 77.1; H = 10.3. (II) C = 77.3; H = 10.2.

$_{22}H_{32}O_4,2H_2O$ requires $H_2O = 6.6$ per cent.

$_{22}H_{32}O_4$ requires C = 77.3; H = 10.1 per cent.

ıs no substance of the empirical formula $C_{22}H_{32}O_4$, having the proper- of this compound, has hitherto been recorded, it is proposed to desig- e it *micromerol*, with reference to the generic name of the plant from ch it has been obtained.

Micromerol is only moderately soluble in cold, but readily in hot alco- , and is therefore easily crystallized from this solvent. It is also mod- tely soluble in ethyl acetate and in acetic acid, but only sparingly so ıcetone, chloroform, and benzene, while in water and in light petro- n it is insoluble. It is likewise insoluble in aqueous alkalis, but if ttle micromerol be dissolved in ether, and the ethereal solution shaken h a solution of sodium hydroxide, a white, insoluble sodium com- nd is at once precipitated. The latter compound, however, is very table, being decomposed through the influence of atmospheric carbon cide with the liberation of the original substance. On the other hand, ıough the micromerol is insoluble in aqueous alkalis, it immediately ses into solution if a few drops of alcohol are added, presumably as ɔmpound soluble in alcohol, for the addition of a drop of hydrochloric l reprecipitates the original substance, whereas the addition of water s not throw it out of solution.

Micromerol is optically active, and its specific rotatory power was de- nined with the following result:

.1609 gram of the anhydrous substance, in 50 cc. of absolute alcohol, e α_D +0° 22′ in a 2 dcm. tube, whence $[\alpha]_D$ +57.0°.

Micromerol is an extraordinarily stable substance. When fused with ıssium hydroxide at a temperature of 270–80° it may be recovered the most part unchanged. A strong solution of chromic anhydride

in acetic acid does not attack it in the cold, and only slowly on heating. A strongly alkaline solution of permanganate very gradually acts upon it in the cold. It is not altered by bromine in chloroform solution, even after heating for several hours, and, therefore, evidently contains no unsaturated linkings. The presence of one hydroxyl group in micromerol was proved by the formation of both a monoacetyl and a monomethyl derivative.

Acetylmicromerol, $C_{33}H_{51}O_4(CO.CH_3)$.—This was prepared by heating the micromerol for a short time with an excess of acetic anhydride, then distilling off the greater portion of the latter, and pouring the product into water, when it solidified immediately. Some difficulty was experienced in crystallizing the product, for it was found that alcohol, which appeared to be best adapted for this purpose, hydrolyzed it quite readily, and unless the crystallization was conducted very rapidly an impure acetyl derivative was obtained. In most of the other usual organic solvents it is extremely soluble. It was ultimately ascertained that the substance could be crystallized from light petroleum containing a small proportion of ethyl acetate, whereby all danger of hydrolysis was averted. From the latter mixture of solvents it separated in fine, colorless needles, melting at 188°.

0.0823 gave 0.2272 CO_2 and 0.0726 H_2O. C = 75.3; H = 9.8.

$C_{33}H_{51}O_4(CO.CH_3)$ requires C = 75.8; H = 9.7 per cent.

$C_{33}H_{50}O_4(CO.CH_3)_2$ requires C = 74.5; H = 9.4 per cent.

For further confirmation respecting the number of acetyl groups in this compound, a weighed quantity of it was hydrolyzed by boiling with aqueous alcohol, and the acetic distillate collected in a standard solution of alkali, which was re-titrated.

0.3261 gave an amount of acetic acid requiring 6.1 cc. N/10 NaOH for neutralization. $CH_3.CO$ = 8.0.

0.3261 gave, on hydrolysis, 0.3002 of $C_{33}H_{52}O_4$. $CH_3.CO$ = 7.7.

$C_{33}H_{51}O_4(CO.CH_3)$ requires $CH_3.CO$ = 7.8 per cent.

The optical rotatory power of this *acetyl derivative* was determined with the following result:

0.0878 gram, dissolved in 25 cc. of chloroform, gave α_D +0° 20′ in a 2 dcm. tube, whence $[\alpha]_D$ +47.1°.

Methylmicromerol, $C_{33}H_{51}O_3.OCH_3,H_2O$.—This was prepared by heating a solution of micromerol in absolute alcohol with an excess of sodium ethoxide and methyl iodide on the water-bath under a reflux condenser. After several hours the reaction was complete, when the greater portion of the alcohol was removed by distillation, and the product poured into water. The precipitated solid was then dissolved in ether, and the ethereal solution washed a few times with strong aqueous alkali, whereby any unchanged micromerol was converted into an insoluble sodium

compound, which could be removed easily by filtration. The ethereal solution was then washed with a little water, dried over calcium chloride, and the ether removed, when the methyl derivative was obtained in a practically pure state.

Methylmicromerol readily crystallizes from alcohol in clusters of thin needles, which contain water of crystallization. The substance, when air-dried, melts at 116–7°, but when rendered anhydrous it melts at 167°.

0.3897 of air-dried substance, on heating at 110° for 2 hours, lost 0.0155 H_2O. $H_2O = 4.0$

(I) 0.1918, dried at 100°, gave 0.5424 CO_2 and 0.1864 H_2O.

(II) 0.1802, dried at 100°, gave 0.5102 CO_2 and 0.1656 H_2O.

(I) C = 77.1; H = 10.8. (II) C = 77.2; H = 10.2.

$C_{33}H_{51}O_3.OCH_3,H_2O$ requires $H_2O = 3.3$ per cent.

$C_{33}H_{51}O_3.OCH_3$ requires C = 77.6; H = 10.3 per cent.

$C_{33}H_{50}O_2(OCH_3)_2$ requires C = 77.8; H = 10.4 per cent.

As the combustion of this substance affords no conclusive evidence respecting the number of methoxyl groups that have entered the molecule, this was established by a separate determination of the methoxyl, for which Perkin's modification of the Zeisel method was employed.[1]

0.2175 gave 0.0993 AgI. $CH_3O = 6.0$.

$C_{33}H_{51}O_3.OCH_3$ requires $CH_3O = 5.9$ per cent.

It may be noted in this connection that the methoxyl group was attacked only with great difficulty by the hydriodic acid, it having been found necessary to heat the mixture for 3 hours at 140° before the reaction was complete. It also follows from the above result that micromerol, $C_{33}H_{52}O_4$, contains no methoxyl group.

Methylmicromerol is readily soluble in the ordinary organic solvents, but insoluble in water.

It was finally deemed desirable to determine the molecular weight of micromerol or one of its simple derivatives, and for this purpose methylmicromerol appeared to be well adapted on account of its ready solubility in cold benzene, whereas micromerol itself is only sparingly soluble in the latter.

0.3339 of anhydrous substance in 26.5 benzene gave Δt —0.121°. M.W. = 510.

$C_{33}H_{51}O_3.OCH_3$ requires M.W. = 526.

Isolation of a New Crystalline Alcohol, Micromeritol, $C_{30}H_{44}O_2(OH)_2,2H_2O$.

The more readily soluble portion of the ether extract of the resins, which, as described under Section II, had been separated by digesting the total amount of this extract with a limited quantity of ether, was examined as follows: The ethereal liquid, which was of a dark green color,

[1] J. Chem. Soc., 83, 1367 (1903).

was first extracted with relatively small quantities of a solution of sodium hydroxide. The first extraction removed a small amount of resinous, uncrystallizable matter, whereas the next few extracts were of an orange-yellow color, and, when acidified, yielded a brown precipitate. The latter was collected, washed, and crystallized from alcohol, from which it separated in yellow, silky needles, melting at 225°. This substance, of which about 1 gram was obtained, was found to be identical with the new phenolic compound, xanthomicrol, $C_{15}H_{12}O_6$, which had been isolated from the aqueous liquid (*A*), as previously described. After all of this yellow substance had been removed by extraction with a solution of sodium hydroxide, further treatment of the ethereal liquid with the same alkali resulted in the formation of a large quantity of an insoluble, dark green sodium compound. The latter was removed by filtration, and the treatment with alkali continued until no more solid substance separated. The ethereal liquid then contained only a small amount of a thick, pitch-like resin, from which nothing crystalline could be obtained.

The above-mentioned solid sodium compound, which amounted to nearly 50 grams, was digested with dilute sulphuric acid, when a substance was liberated which was collected on a filter at the pump and well washed with water. The solution of this substance in hot alcohol was treated with animal charcoal for the purpose of removing some green coloring matter when, after filtration, a faintly yellow liquid was obtained, which was set aside to crystallize. The first deposits from this liquid were not of a distinctly crystalline character, and melted somewhat indefinitely at about 250°. They were found, however, to contain appreciable quantities of the previously described micromerol, $C_{33}H_{52}O_4$, since by treatment with an amount of ether which was insufficient to dissolve the whole, and recrystallizing the undissolved portion from alcohol, fine colorless needles were obtained which melted at 277°, and were identical with the compound previously isolated.

The alcoholic liquid from which the above-mentioned first deposits had been removed, together with the alcoholic solution of that portion of these deposits which was more readily soluble in ether, was concentrated. A gelatinous mass was first obtained, from which a further small quantity of micromerol was isolated. The mother-liquors from this gelatinous substance were further concentrated, when, after long standing, feathery needles separated which were different in character from the previously isolated micromerol. Some difficulty was experienced in isolating this compound in a pure state on account of its being accompanied by a little amorphous, fluffy matter. It was found, however, that by allowing the substance to crystallize slowly from a dilute solution it could be obtained in well-formed crystals, and by means of

fine muslin filter these were easily separated from the amorphous im-
ırities, which passed through the filter with the mother-liquors. The
bstance, after washing with a little alcohol and recrystallizing from
e same solvent, was finally obtained pure. It then melted at 294-
', when rapidly heated. On analysis it gave the following results:
0.2144 of air-dried substance, when heated for 2 hours at 110°, lost
0158 H_2O. $H_2O=7.4$.
(I) 0.1623 of anhydrous substance gave 0.4537 CO_2 and 0.1488 H_2O.
(II) 0.1416 of anhydrous substance gave 0.3945 CO_2 and 0.1275 H_2O.
(I) C=76.2; H=10.2. (II) C=76.0; H=10.0.
$C_{20}H_{40}O_4$, $2H_2O$ requires $H_2O=7.1$ per cent.
$C_{20}H_{40}O_4$ requires C=76.6; H=9.8 per cent.
This substance evidently possesses the empirical formula $C_{20}H_{40}O_4$,
ıd as no substance of this formula, with the same properties, has hither-
been recorded, it must be regarded as a new compound. It is there-
re proposed to designate it by the distinctive name, *micromeritol*, with
ference to the botanical name of the plant from which it has been
tained.
Micromeritol is moderately soluble in cold, and readily soluble in hot
ohol, from which, on cooling, it crystallizes in clusters of fine, color-
s needles. It is also readily soluble in chloroform and ethyl acetate,
it only moderately soluble in benzene. In water and in light petro-
ım it is insoluble. It is optically active, and a determination of its
ecific rotatory power gave the following result:
0.0543 gram of the anhydrous substance in 25 cc. of chloroform gave
, +0°16′ in a 2 dcm. tube, whence $[\alpha]_D$ +61.4°.
Micromeritol, in its general characters, resembles micromerol. It
for example, insoluble in aqueous alkalis, but readily yields an un-
ıble sodium compound on shaking an ethereal solution of the sub-
ınce with aqueous sodium hydroxide. Unlike micromerol, from which
differs by the elements C_3H_8, it contains two hydroxyl groups. The
ter, however, are dissimilar in character, for if the diacetyl derivative
boiled with aqueous alcohol, one of the acetyl groups is eliminated
ile the other remains unaffected.
A property of the above-described alcohols, which is also possessed
a greater or less extent by others of a similar character and represented
the same general formula, $C_nH_{2n-14}O_4$, is that of forming colloidal
utions. If, for example, a little micromerol, $C_{23}H_{32}O_4$, be dissolved
boiling ethyl alcohol, a little ammonia added, and the liquid heated
til the alcohol and ammonia have been for the most part removed, no
ecipitate is produced on diluting the cooled liquid with water. This
ar liquid, on being allowed to stand for about an hour, forms a per-
tly transparent jelly. When, however, an aqueous solution of an

electrolyte, such as ammonium chloride, is added to the liquid before it has formed a jelly, the micromerol is immediately precipitated in a flocculent form. In the case of micromeritol, $C_{30}H_{46}O_4$, a slight precipitation was produced on the addition of water and the solid separated completely in a crystalline state on allowing the liquid to stand for some time, whereas complete precipitation immediately ensued on the addition of a drop of a solution of ammonium chloride. On testing the monohydric alcohol lippianol,[1] $C_{25}H_{36}O_4$, in the same manner, it was found that on diluting the ammoniacal liquid with water a crystalline precipitate was immediately produced, and the amount of this was not increased by the addition of a solution of ammonium chloride. The alcohol, morindanol,[2] $C_{28}H_{42}O_4$, when tested under the same conditions, exhibits a behavior very similar to that of micromerol, with perhaps still less tendency to deposit the solid substance except when an electrolyte is added. The tendency to the formation of these colloidal solutions, therefore, evidently increases in proportion to the molecular weight of the substance.

Di-acetylmicromeritol, $C_{30}H_{44}O_4(CO.CH_3)_2$. — When micromeritol is subjected for a short time to the action of boiling acetic anhydride, and the solution allowed to cool, the *di-acetyl derivative* separates in long, colorless needles, which melt at 204°. It can also be crystallized from ethyl acetate or from alcohol, and separates from the latter solvent in glistening plates.

0.1611 gave 0.4350 CO_2 and 0.1312 H_2O. C = 73.6; H = 9.0.

$C_{30}H_{44}O_4(CO.CH_3)_2$ requires C = 73.6; H = 9.0 per cent.

The molecular weight of the di-acetyl derivative was determined by the cryoscopic method with the following result:

0.3308 in 21.2508 benzene gave Δt —0.15°. M.W. = 509.

$C_{30}H_{44}O_4(CO.CH_3)_2$ requires M.W. = 554.

The somewhat low result of this determination is probably due to the facility with which the di-acetyl derivative loses some of its acetic acid. It, nevertheless, suffices to show that micromeritol possesses the molecular formula assigned to it.

Mono-acetylmicromeritol, $C_{30}H_{45}O_4(CO.CH_3)$.—If di-acetyl micromeritol be boiled with aqueous alcohol for a short time it loses one acetyl group, and the solution, on cooling, deposits thin, colorless needles of a *mono-acetyl compound*, which melts with decomposition at 255°. 0.3090 of the di-acetyl derivative gave 0.2846 of the mono-acetyl compound. Loss = 7.9 per cent.

$C_{30}H_{44}O_4(CO.CH_3)_2 \rightarrow C_{30}H_{45}O_4(CO.CH_3)$ requires a loss of 7.6 per cent.

Mono-acetylmicromeritol is readily soluble in chloroform, and moderately soluble in alcohol, ethyl acetate, and benzene.

[1] Amer. J. Pharm., 79, 455 (1907).

[2] J. Chem. Soc., 91, 1918 (1907).

[I, IV and V. *Chloroform, Ethyl Acetate and Alcohol Extracts of the Resins.*

The portion of resin extracted by chloroform (III) was relatively nall in amount, and formed a hard, black, brittle mass. It consisted f a complex mixture of amorphous substances, and, with the exception f a very small quantity of micromerol, nothing of a crystalline nature ould be isolated from it.

The portions of resin extracted by ethyl acetate (IV) and alcohol V) respectively, likewise consisted of mixtures of black, amorphous ubstances. They were dissolved in amyl alcohol and the solutions xtracted with sodium carbonate, but nothing of a crystalline character ould be separated from them.

Summary.

The results of this investigation have shown that *Micromeria Chamisnis* (Benth.) Greene (syn. *M. Douglassi*, Benth.), commonly known s "Yerba Buena," contains, in addition to some essential oil, resins, nd other amorphous substances, the following compounds:

1. *Xanthomicrol*, $C_{15}H_{10}O_4(OH)_2$, a new phenolic substance, which rystallizes in fine, lemon-yellow needles, melting at 225°. It yields a *i-acetyl derivative*, $C_{15}H_{10}O_6(CO.CH_3)_2$, which crystallizes in pale yellow eedles, melting at 116°.

The amount of xanthomicrol obtained corresponds to about 0.02 per ent. of the weight of air-dried plant.

2. *Micromerol*, $C_{33}H_{51}O_3$–OH,$2H_2O$, a new monohydric alcohol, hich crystallizes in fine, colorless needles, melting at 277°. It is opically active, having $[\alpha]_D$ +57°. Its *acetyl derivative*, $C_{33}H_{51}O_4(CO.CH_3)$, rms colorless needles, which melt at 188° and have $[\alpha]_D$ +47.1°. Its *ethyl derivative*, $C_{33}H_{51}O_3.OCH_3,H_2O$, crystallizes in thin needles, which elt at 116-7° or, when anhydrous, at 167°.

The amount of micromerol obtained corresponds to about 0.25 per nt. of the weight of air-dried plant.

3. *Micromeritol*, $C_{30}H_{44}O_2(OH)_2,2H_2O$, a new dihydric alcohol, which ystallizes in fine, colorless needles, melting at 294-6°. It is optically tive, having $[\alpha]_D$ +61.4°. Its *di-acetyl derivative*, $C_{30}H_{44}O_4(CO.CH_3)_2$, nd *mono-acetyl derivative*, $C_{30}H_{45}O_4(CO.CH_3)$, form colorless needles, hich melt respectively at 204° and 255°.

The amount of micromeritol obtained corresponds to about 0.05 per nt. of the weight of air-dried plant.

4. Hentriacontane, $C_{31}H_{64}$ (m. p. 66-7°), about 0.05 per cent., with pparently a very small amount of pentatriacontane.

5. A Phytosterol, $C_{27}H_{46}O,H_2O$ (m. p. 135°), in small amount.

6. Glycerides of palmitic, arachidic, and behenic acids.

7. Formic, acetic, and butyric acids in a free state.

8. Glucose (phenylglucosazone, m. p. 217°), a considerable amount.

The total amount of crude resin corresponded to 3.5 per cent. of the weight of the plant, and from it most of the above-described crystalline substances were isolated.

The amount of essential oil obtained by the direct distillation of the air-dried plant corresponds to 0.16 per cent. of the weight of the latter. This oil had a pale yellowish brown color, an agreeably aromatic, mint-like odor, and possessed the following constants: $d=0.9244$ at 20°; $[\alpha]_D$ —22°48′ in a 1 dcm. tube.

Among the above-mentioned substances the two crystalline alcohols, micromerol and micromeritol, are of special interest. Their empirical composition is represented by the same general formula $C_nH_{2n-14}O_4$, and, as they contain no unsaturated linkings, they are evidently cyclic compounds in which a benzene nucleus is doubtless present. As micromerol contains but one hydroxyl group, whereas micromeritol contains two such groups, they are not simple homologues, but a similarity in their general characters renders it probable that some fundamental relationship exists between them. It is of further interest to note that a crystalline, monohydric alcohol, $C_{25}H_{36}O_4$ (m. p. 300-8°; $[\alpha]_D$ + 64.9°), designated as lippianol, which was recently isolated from a South African plant, *Lippia scaberrima*, Sonder (Nat. Ord. *Verbenaceae*), possesses the same general formula as those above mentioned, namely, $C_nH_{2n-14}O_4$, and has similar properties (compare Power and Tutin, *Archiv der Pharm.* **245**, 344 (1907), and *Amer. J. Pharm.*, **79**, 449 (1907)). Another compound of this class, having the formula $C_{38}H_{62}O_4$ (m. p. 278°; $[\alpha]_D$+65.9°), and designated morindanol, has likewise been isolated in these laboratories from a West African plant, *Morinda longiflora*, G. Don (Nat. Ord. *Rubiaceae*). Cf. *J. Chem. Soc.*, **91**, 1918 (1907).

Our thanks are due to Mr. H. H. Dale, Director of the Wellcome Physiological Research Laboratories, for having conducted a test with micromerol. One gram of the substance was administered to a small dog, but no symptoms of any kind were manifested, and it therefore appears to be devoid of any pronounced physiological activity.

MARRUBIIN.[1]

By H. M. Gordin.

Received November 22, 1907.

The bitter principle, marrubiin, was discovered in horehound (*Marrubium vulgare*, Linné) by Mein and, without indicating the method by which it was obtained from the plant, sent to Harms for investigation.[2] Later

[1] The Wm. S. Merrell Chem. Co. deserves my thanks for not only supplying the horehound but for preparing for me an extract in accord with my directions.

[2] Arch. Pharm. (2), **83**, 144; (2), **116**, 141.

the bitter principle was examined by Kromayer,[1] Hertel,[2] Morrison[3] and Matusow.[4] The different chemists employed different methods for the isolation of marrubiin, and their results differ so much from each other that it seemed advisable to undertake a thorough examination of this constituent of a popular plant. As marrubiin is only sparingly soluble in water, the yield obtained by this menstruum is extremely small. This accounts for the very small yield obtained by Harms (2 grams from 25 lbs.). On the other hand, owing to the great expense involved, ether, while a fairly good solvent for the bitter principle, is not suitable for extraction on a large scale. It seemed, therefore, that Matusow's method in which acetone is used as a menstruum was the most convenient for the purpose. Matusow's method consists in extracting the horehound with acetone, distilling off the solvent and treating the residue with hot benzene. According to Matusow, the benzene solution on cooling deposits the marrubiin in crystalline condition. I have faithfully followed Matusow's directions and obtained the crystals, but a careful examination of these showed them to be not marrubiin but potassium nitrate. The identity of the salt was established by a large number of the reactions of both the metallic and the nitrate ions, as also by a crystallographic comparison with pure potassium nitrate carried out by Prof. Kraus, of the University of Michigan. The appearance of saltpeter in considerable quantities in the acetone extract is possibly due to the presence of water in ordinary acetone. The small crystals of the salt cannot be noticed in the very dark residue left after distilling off the acetone; when the residue is heated with benzene the potassium nitrate, which is extremely easily soluble in hot water, goes into solution in the small amount of water present and crystallizes out upon cooling. Having failed to prepare marrubiin by Matusow's method, I worked out the following method. The coarsely ground horehound is extracted by percolation with cold acetone till the latter comes out nearly tasteless, the solvent distilled off and the residue digested repeatedly with considerable quantities of petroleum ether. After pouring off the petroleum ether the residue is digested several times with warm water to remove soluble inorganic salts and then dissolved in just enough hot alcohol to bring all into solution. On cooling, the whole liquid solidifies to a mass of crystals. After washing the crystals with cold alcohol, they are repeatedly recrystallized from hot alcohol, using animal charcoal freely, till their color is snow-white and their melting point is constant. The yield of pure marrubiin by this method was 0.25 per cent.; but as it had to be recrystallized nearly a dozen times and marrubiin

[1] Arch Pharm., 108, 258.
[2] Am. J. Pharm., 1890, 273.
[3] *Ibid.*, 1890, 327.
[4] *Ibid.*, 1897, 201.

is quite soluble in cold alcohol, most of it remained in the mother liquors, from which I hope to obtain additional quantities. The melting point of marrubiin is 154.5–155.5°; under a pressure of 15 mm. it boils at 297–99°. It crystallizes from hot alcohol in two different forms. On quickly cooling the alcoholic solution the crystals are small and fine; by slow crystallization large heavy crystals can be obtained. If the hot saturated solution is free from any solid marrubiin, the solution can be kept for several hours in a supersaturated condition, and when crystallization begins, the crystals are flat and over two centimeters long. As shown by the melting point and analysis, the two modifications are chemically identical. A complete separation of the two modifications could not be effected. Following is an account of crystallographic measurements carried out by Prof. Kraus:

"Marrubiin crystallizes in two distinct modifications from a solution in alcohol. The crystals of the first modification are well developed and allowed accurate goniometric measurements to be made. The second modification does not show as well developed faces, so that for the present only approximate measurements for several angles can be given.

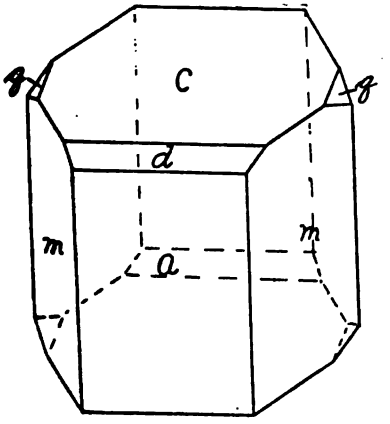

Fig. 1.

"*Modification One.* — These crystals are readily obtained by slow evaporation of an alcoholic solution. The crystals are usually quite small, about 2 mm., perfectly clear, and transparent. The following forms were observed: *a* (100), *m* (110), *c* (001), *d* (101), and *q* (011). Of these forms the ortho pinacoid *a* (100) and the prism *m* (110) are usually quite large, giving rise to a prismatic development. The basal pinacoid *c* (001) may, however, predominate, causing the tabular habit to result. The domes *d* (101) and *q* (001) are generally quite small but give excellent images. Fig. 1 shows the usual combination and development. In all, eight crystals were measured with the following results:

"Crystal System—Monoclinic.

"Axial Ratio—$a : b : c = 1.5551 : 1 : 0.885$, $\beta = 61° 17'$.

	Observed.	Calculated.
$a:m$ = (100): (110) =	53° 45′	....
$a:c$ = (100): (001) =	61° 17′	....
$c:q$ = (001): (011) =	37° 49′	....
$a:d$ = (100): (101) =	39° 51.3′	39° 55.7′
$c:m$ = (001): (110) =	73° 32.5′	73° 29.5′

"*Modification Two.*—The second modification also belongs to the monoclinic system. The crystals are flat tabular in development and show a prism angle of 94° 36′. The angle between the ortho- and basal pinacoids, *a* (100) and *c* (001), is about 71° 3.5′. More accurate measurements will be made later. The above values are, however, sufficient to show a decided difference in the crystallization of the two modifications.

EDWARD H. KRAUS."

The formula of marrubiin is $C_{21}H_{28}O_4$. Analysis gave C, 73.00, 73.14, 72.90, 72.97; H, 8.28, 8.57, 8.32, 8.43; calculated for $C_{21}H_{28}O_4$; C, 73.21, H, 8.20. A molecular weight estimation by the cryoscopic method with phenol as solvent gave M = 327. Calculated for $C_{21}H_{28}O_4$; 344.22. Marrubiin is isomeric with the menthyl ester of acetoxy α-phenylacrylic acid and with the menthyl ester of benzoylacetic acid, which were prepared by Lapworth and Hann.[1] The first of these esters melts at 51–52°, the second is a liquid. Marrubiin is dextrorotatory. $[\alpha]_D^{24} = 45.68°$ ($c = 4.794$, solvent, acetone from bisulphite and redistilled by myself). The polariscope was a Josef and Jan Frič apparatus. Marrubiin is soluble in about 60 parts of alcohol at 20° and 20,835 parts of water at 21.5°. It is very easily soluble in acetone, chloroform, hot alcohol, warm phenol, pyridine and warm glacial acetic acid; difficultly soluble in ether or benzene. It does not reduce Fehling's solution or ammoniacal silver nitrate either before or after warming with dilute mineral acids. It does not contain CH_3O groups (by Zeisel's method) and does not decolorize bromine in glacial acetic acid solution. It has a very bitter taste and a neutral reaction. It does not react with acetic anhydride, benzoyl chloride, hydroxylamine or phenylhydrazine, showing absence of hydroxyl or carbonyl groups. In all cases unchanged marrubiin was recovered as shown by crystalline appearance, melting point and bitter taste. Cold aqueous or alcoholic potassium hydroxide has no effect upon it. Very dilute alcoholic potassium hydroxide attacks it slowly on prolonged boiling. When boiled for a short time with ten per cent. alcoholic potassium hydroxide it takes up a molecule of water and is quantitatively converted into the potassium salt of a new acid which I have named marrubic acid, $C_{20}H_{29}O_3.CO_2H$. The acid is made as follows: Ten grams marrubiin are boiled for about half an hour with 150 cc. of alcohol containing 10 to 12 per cent. of potassium hydroxide, the liquid is then diluted with twice its volume of water and concentrated till the odor of alcohol disappears, adding water from time to time. The solution is set aside in a cool place for 24 hours, and the very small amount of slimy matter which separates out removed by filtration. The filtrate is acidified with hydrochloric acid and the extremely bulky white precipitate which separates out, collected on a filter, thoroughly washed with water and recrystallized from hot alcohol to which hot water is gradually added. Yield over 98 per cent. of the theoretical. Thus obtained marrubic acid forms snow-white, long silky needles. The acid is extremely bulky and looks like quinine sulphate or caffeine, but is even fluffier than these. According to Prof. Kraus the acid crystallizes in extremely fine, long, prismatic crystals. The prism faces show, apparently, parallel extinction. The acid melts at 173–4°. Its formula

[1] J. Chem. Soc., 81, 1497 and 1507.

is $C_{20}H_{29}O_3.CO_2H$. Analysis gave: C, 69.02, 69.08; H, 8.76, 8.67. Calculated for $C_{20}H_{29}O_3.CO_2H$: C, 69.57; H, 8.35. Marrubic acid is very easily soluble in alcohol, warm phenol and pyridine, difficultly soluble in ether, glacial acetic acid and benzene, almost insoluble in water. It has an acid reaction in alcoholic solution. It is isomeric with antiarigenin. The latter is not an acid and becomes intensely yellow at 170° melting at 180°. Marrubic acid is very easily soluble in ammonia water, but upon concentration of the solution all the ammonia evaporates, leaving the acid unchanged. It is easily soluble in alkalies and alkali carbonates and forms salts with metals, none of which, however, could be obtained in crystalline condition. The salts all seem to be very easily soluble in water and alcohol with the exception of the copper salt, which is amorphous and difficultly soluble in water. Titration with standard alkali showed the acid to be monobasic. 0.2200 gram of the acid required 6.05 cc. N/10 KOH (phenolphthalein as indicator), and 0.3963 gram required 10.8 cc. N/10 KOH. Calculated for $C_{20}H_{29}O_3.CO_2H$, 6.1 and 10.9 cc. respectively.

Barium marrubate, $(C_{20}H_{29}O_3.CO_2)_2Ba$, was prepared by digesting marrubic acid with an excess of barium carbonate in dilute alcohol, filtering, concentrating to a small bulk, again filtering (to remove traces of barium carbonate) and evaporating to dryness. The salt is amorphous and very easily soluble in water or alcohol but insoluble in ether. It could not be obtained in crystalline form. For analysis it was converted into barium carbonate. 0.2818 gram gave 0.0645 g. $BaCO_3$, and 0.5605 g. gave 0.1293 g. $BaCO_3$. Calculated for $(C_{20}H_{29}O_3.CO_2)_2Ba$, 15.97 per cent. Ba. Found: 15.93 and 16.06 per cent. Ba. At water bath temperature marrubic acid quickly reduces ammoniacal silver nitrate or Fehling's solution. Neither the alcohol solution of the free acid nor the aqueous solution of the barium salt are colored by ferric chloride. Marrubic acid is dextrorotatory. $[\alpha]_D^{21.5} = 7.86$. ($c = 2.5456$; solvent, acetone).

When heated to 190–200° under a pressure of 15 mm. the acid boils up suddenly, loses one molecule water and changes back to marrubiin. This was shown by treating the melt with dilute sodium carbonate solution to remove traces of unchanged acid and recrystallizing the insoluble part from alcohol. The crystals were insoluble in alkali carbonates and melted at 154–5°. The same reconversion of marrubic acid into marrubiin can be effected by warming the acid with ten times its amount of acetic anhydride and a trace of zinc chloride for a few minutes to about 50°. On largely diluting the liquid, which assumes a dark yellow color, the color disappears and an oily liquid separates out, which on standing under water becomes solid. The solidified precipitate was digested with sodium carbonate and then recrystallized from alcohol. It was

alkali carbonates and melted at 154–5°. The liquid ob-
digestion with sodium carbonate gave no precipitate upon
excess of acid; hence the reconversion of marrubic acid into
›y this method is quantitative. The acid is also reconverted
›iin by boiling for an hour with alcoholic hydrochloric acid
er cent. acid and 50 cc. alcohol). On throwing the solution
water and recrystallizing the precipitate from alcohol, it was
e marrubiin (insoluble in alkali carbonates and melted at
Part of the acid is resinified in this reaction. On digest-
ion of marrubic acid in pyridine with benzoyl chloride (one
ch) for 24 hours and then adding 750 cc. water an oily liquid
ut which becomes solid upon long standing. The mass was
th dilute sodium carbonate solution and then recrystallized
ol. It was found again to be marrubiin. It constituted
er cent. of the amount of acid taken. The part soluble in
bonate does not seem to be unchanged marrubic acid. It
tated from the alkaline carbonate solution by addition of
c acid and recrystallized from alcohol to which hot water
lly added. On standing fine needles separated out. They
ween 164–70° and represented most probably a benzoyl
of marrubic acid, but the amount was too small for an analy-

rrubate.—Marrubic acid was digested with a solution of potas-
xide on the water bath, leaving the acid in slight excess, the
ed to remove undissolved acid and evaporated to dryness.
s of the potassium salt thus obtained were mixed with 4 cc.
and 20 cc. acetone and the mixture boiled for two and a half
r reflux condenser. The liquid was then evaporated to dry-
esidue treated with dilute sodium carbonate solution to re-
ble traces of unchanged acid and recrystallized by dissolv-
alcohol and adding water to turbidity. As the sodium car-
tion did not give any precipitate with acids, the esterifica-
rrubic acid by this method must be quantitative. From a
alcohol and water the ester crystallizes in very pretty glitter-
from a mixture of ether and petroleum ether large heavy
1 be obtained, which consist of layers of leaflets. Unlike
nd marrubic acid, the ethyl ester is tasteless. It is extremely
le in ether and pyridine, a little less soluble in alcohol, chloro-
zene and still less in petroleum ether. It melts at 87°. When
›out 100° under a pressure of 28 mm. it boils, gives up a mole-
ohol and is reconverted into marrubiin. This was shown
llizing the reaction product from alcohol and comparing
rrubiin. For analysis an ethoxyl estimation was made by

Zeisel's method. Found: 10.78 and 11.50 per cent. of C_2H_5O. Calculated: 11.54 per cent. of C_2H_5O. The ester forms an acetyl derivative, but this and several other derivatives of marrubiin will be reported upon in my next paper. The results of the investigation so far show that marrubiin is a lactone behaving like a γ-lactone in that it easily takes up a molecule of water and changes to a hydroxy acid. The formulae of marrubiin, marrubic acid and ethyl marrubate can therefore be written as follows:

$$C_{20}H_{28}O_2{-}CO, \qquad C_{20}H_{28}O_2(OH).COOH, \qquad C_{20}H_{28}O_2(OH)COO.C_2H_5.$$

The investigation is continued.

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DECOMPOSITION CURVES OF SOME NITROCELLULOSES OF AMERICAN MANUFACTURE.[1]

BY OSWIN W. WILLCOX.

Received November 11, 1907.

In the course of a study of the test proposed by Obermuller[2] for the stability of nitrocellulose, it was observed that the rate of decomposition of an ordinary collodion cotton during a given period of time depended on whether or not the gaseous products of decomposition had been allowed to remain in contact with the sample during previous periods. As the Obermuller apparatus is perhaps the most accurate and convenient means yet devised for following quantitatively the progress of the decomposition of a nitrocellulose at temperatures below its ignition point, some of the results obtained are deemed of interest.

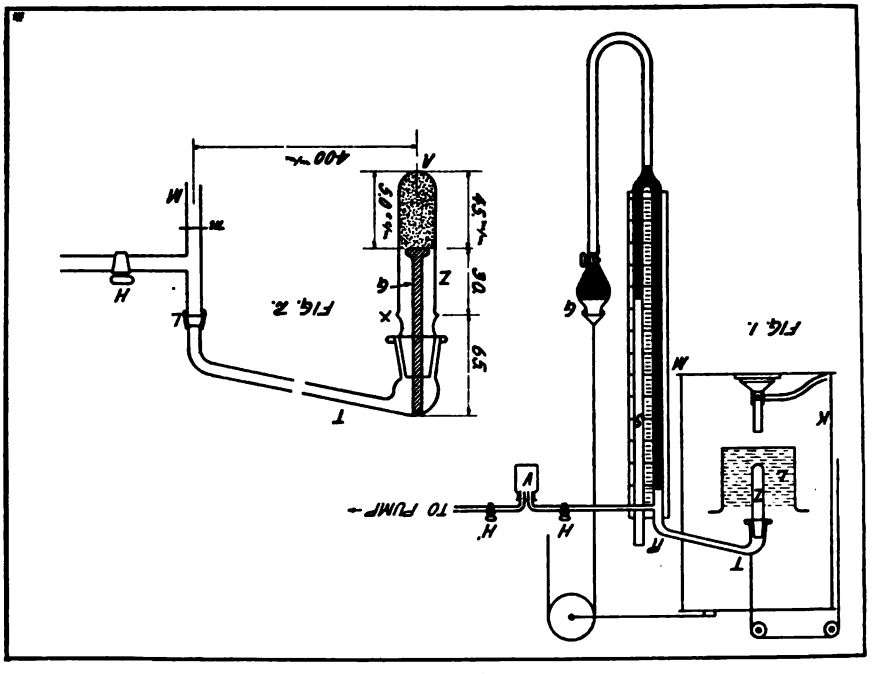
Obermuller's test is essentially as follows: A weighed quantity of the nitrocellulose to be tested is placed in a glass tube, which is then evacuated by means of a good air pump. When the air has been removed as much as possible, the tube is plunged into a bath previously brought to a standard temperature, which is maintained constant throughout the duration of the test. The nitrocellulose in the tube immediately begins to decompose and to give off gaseous products; the tube being in connection with a mercury manometer, the rate at which the products of decomposition are evolved is measured by the increase of pressure shown by the manometer. This rate will naturally be greater for nitrocellulose of poor stability and less for nitrocellulose of good stability. Working at a standard temperature of 140° C., and with a tube which, with its connections, had a volume of 37 cc., Obermuller

[1] Published by permission of the Honorable the Secretary of War.

[2] Mittheilung aus dem Berliner Bezirksverein des Vereins deutscher Chemiker, October 11, 1904.

found that one gram of a stable nitrocellulose does not cause in one hour a greater increase of pressure than 100 mm. of mercury.

The apparatus employed is diagrammatically shown in Figs. 1 and 2, which are copied from Obermuller's paper. The decomposition tube



Figs. 1 and 2.

Z (Fig. 1) is of glass and of about 12 cc. capacity; the top of Z is ground to fit the larger end of T, by means of which it is connected to the manometer M. Behind the manometer is a scale S. By means of the side tube R the decomposition tube can be put in communication with the air pump. V is a glass bottle, on either side of which is a glass stopcock (H and H′). The lower part of the manometer is connected with the mercury reservoir G. The bath, L, which may consist of a saturated solution of calcium chloride, or, better, of oil, such as is used in the cylinders of locomotives, serves to heat the tube Z. The sheet-iron case K, which is provided with a window of heavy glass, serves to protect the operator from possible explosions. In Fig. 2 is shown an enlarged sketch of the tube Z and its connections. G is a glass rod sealed by its upper end to T; the object of this rod is to hold the nitrocellulose in place in the lower end of Z. X is a mark 1 cm. under the cap.

The method of procedure adopted in this study is as follows: Exactly 2 grams of the nitrocellulose previously dried by heating for 1 hour at 100° were placed in the decomposition tube Z; any nitrocellulose

adhering to the walls of the tube were swept down by means of a small wad of pure dry absorbent cotton, which was allowed to remain in the tube during the heating. The tube was then fitted in place and evacuated as completely as possible, usually down to an internal pressure of less than 5 mm. of mercury. The bath having been brought to 140° the positions of the mercury in both limbs of the manometer were noted, all stopcocks were closed and the tube lowered into the bath up to the mark X, the time being noted at the same instant. Exactly 15 minutes from the time of immersing the tube, the surface of the mercury in the left limb of the manometer was brought back to its original position and the rise of the mercury in the right limb was noted; and this was repeated at intervals of 15 minutes until four such readings had been taken. The accumulated gases were now pumped out and a vacuum maintained in the tube for 15 minutes. At exactly 75 minutes from the time of beginning all stopcocks were again closed and the gaseous products of decomposition allowed to accumulate for a period of 15 minutes. The pressure developed during these 15 minutes was read, the tube again kept vacuous for 15 minutes, and so on alternately for 5 hours from the time of beginning. For convenience in discussion, the whole time of heating may be regarded as divided into periods of 15 minutes each. During the first four periods the gases were allowed to accumulate in the tube and to exert pressure; after the first hour the gases were being continually withdrawn during the odd periods, whereas they were allowed to accumulate during the even periods. The procedure followed during the first hour will be referred to as "test with increasing initial pressure," and that followed after the first hour as "test with constant initial pressure." All readings of pressure are given as millimeters of mercury per gram of substance. The data obtained are tabulated in Table I.

TABLE I.

Pressure in mm. of mercury per period of 15 minutes.

No. of sample.	Test with increasing initial pressure.				Test with constant initial pressure.							
	1st.	2nd.	3rd.	4th.	6th.	8th.	10th.	12th.	14th.	16th.	18th.	20th.
2920	20.3	23.9	28.7	32.9	27.8	28.6	30.6	31.0	33.5	33.0	33.5	34.0
3831	18.7	23.4	27.7	33.0	27.7	28.7	30.6	31.3	33.7	32.7	34.5	34.5
3883	18.6	22.2	27.8	32.0	27.6	28.2	30.3	30.6	32.2	32.5	33.0	33.5
3863	21.0	29.5	35.0	42.7	38.0	39.7	41.8	43.3	45.7	45.7	47.0	47.5
3607	21.9	24.5	28.7	34.2	31.5	33.5	34.1	34.5	36.7	36.2	39.0	38.0
3608	19.2	20.9	24.6	29.1	25.5	27.0	28.1	29.1	29.7	31.7	31.5	32.5
3609	18.1	22.2	25.8	25.8	29.4	26.1	28.5	28.3	29.5	29.7	32.0	32.0

The samples of nitrocellulose here reported on represent the product of the principal factories of the United States. They are "decanitrocelluloses" of about 12.60 per cent. nitration and 99 per cent. solubility in ether alcohol.

The figures at the top of the columns in Table I are the numbers of the periods, of 15 minutes each, during which the gases were allowed to accumulate (it will be remembered that a vacuum was maintained in the tube during the odd periods). The results are also plotted in the accompanying curves. An examination of the figures given in Table

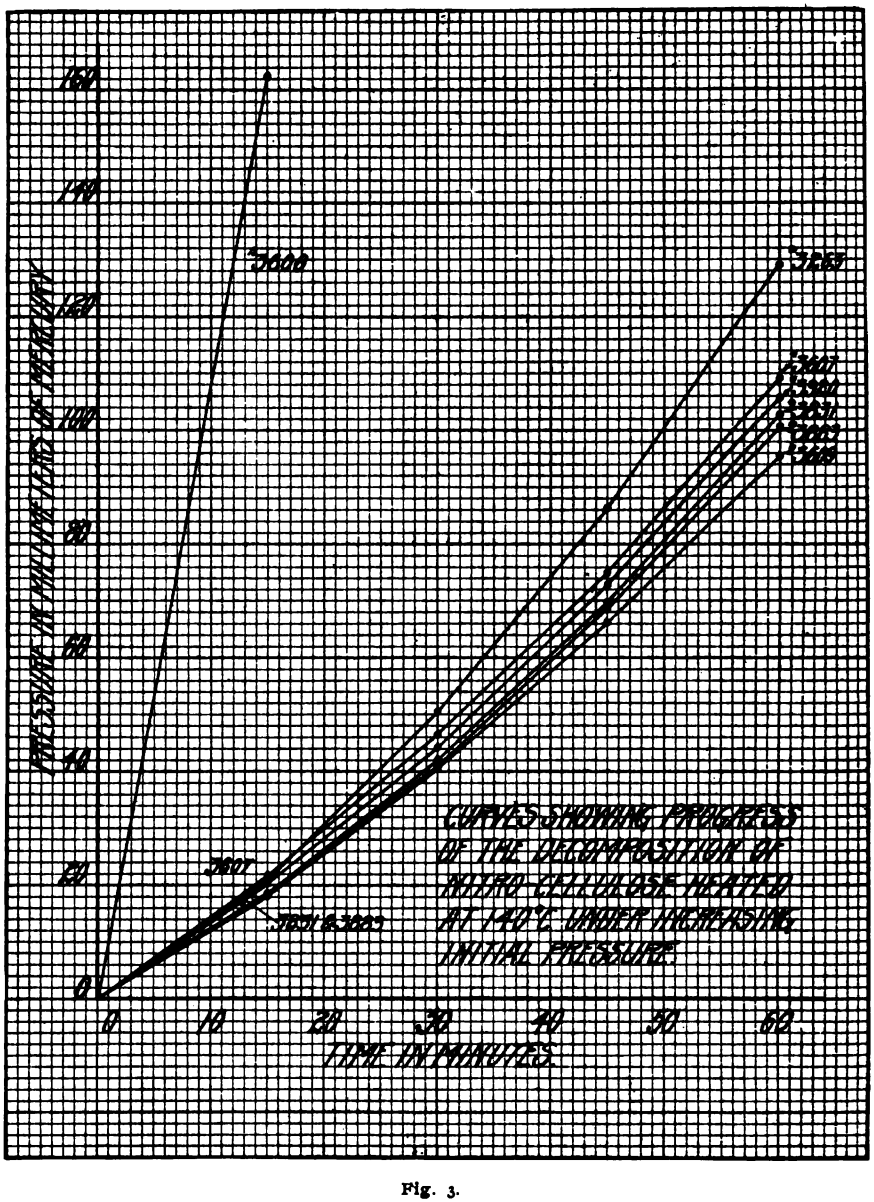


Fig. 3.

Fig. 4.

I will show that the course of the decomposition in "test with increasing initial pressure" and in "test with constant initial pressure" follows different laws. In the case of sample No. 3831, for example, the quarter hourly increase of pressure in the first period is 18.7 mm., in the second 23.4 mm., in the third 27.7 mm., and in the fourth 33.0 mm., an average constant difference of about 4.5 mm. By the aid of this law of increase it may be calculated that during the sixth period the increase of pressure would be 42 mm., if the gases were allowed to accumulate in the tube without interruption. The calculated rate for the sixth period was found by experiment to be the actual rate under the condition named. If, however, a vacuum be maintained in the tube during the fifth period, then the increase of pressure during the sixth period is not 42 mm., but only 27.7 mm., a difference of 14.3 mm. The difference in the rates of increase of pressure under the two conditions measures the catalytic effect of the presence of the gaseous products of decomposition on the speed of the reactions of decomposition. It may be noted that while removal of the gases lowers the "decomposition pressure" of the heated nitrocellulose it is not restored to the original value; the initial decomposition pressure gradually rises with the time of heating.[1]

[1] At the same time the heated nitrocellulose is being transformed into a modification soluble in absolute alcohol. A separate report, with quantitative data, will be made on this subject in the future.

The results reported in Table I were obtained by working at a constant volume of 30 cc. It is obvious that as the volume of the tube and its accessories determines the concentration of the gaseous products of decomposition, the rate of increase of pressure will vary with this volume. To deduce the volume relations of the test a number of exper-

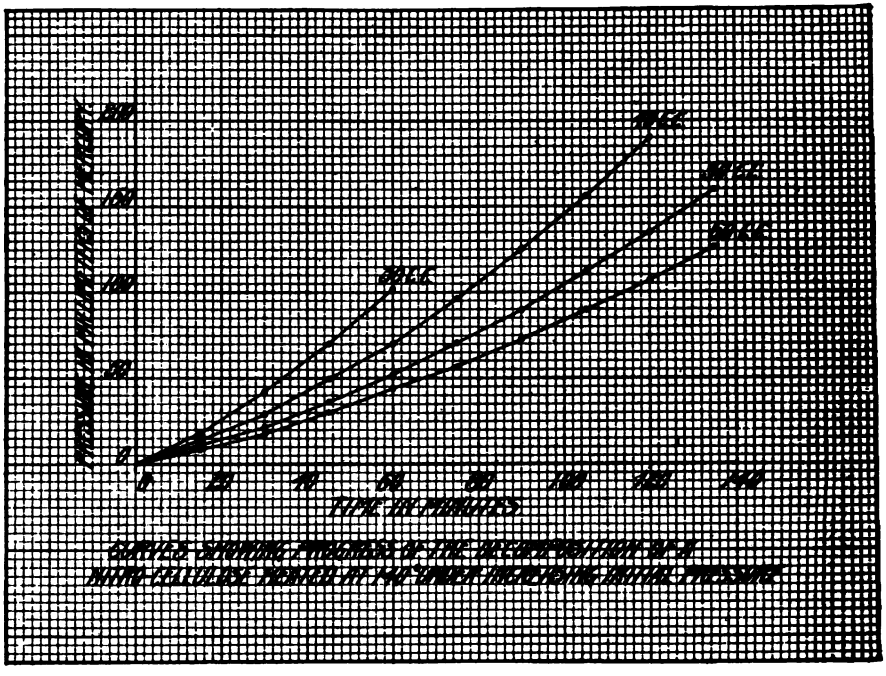


Fig. 5.

iments were made on sample No. 3831. The total volume of the apparatus as far as the glass cock H′ was measured and found to be 60 cc. On leaving H open during a determination, the gases would exert a pressure corresponding to this volume. By adding 10 cc. of mercury to the glass bottle V, the volume could be reduced to 50 cc., another 10 cc. of mercury would reduce it to 40 cc., and so forth. The pressures obtained by working at the volumes 30 cc., 40 cc., 50 cc., and 60 cc. are given in

TABLE II.

OBERMULLER TEST AT DIFFERENT VOLUMES.

Pressure in mm. of mercury per period of 15 minutes.

Volume in cc.	Test with increasing initial pressure.				Test with constant initial pressure.							
	1st.	2nd.	3rd.	4th.	6th.	8th	10th.	12th.	14th.	16th.	18th.	20th
30	18.7	23.4	27.7	33.0	27.7	28.7	30.6	31.3	33.7	32.7	34.5	34.5
40	12.5	17.0	19.5	22.0	21 0	21.0	23.0	25.0	24.5	24.5	26.5	25.5
50	10.0	12.5	15.0	16.0	15.5	17.0	17.5	17.5	18.5	19.5	20.5	21 0
60	8 0	9.5	12.0	13.5	13.5	14.6	15.5	15.0	15.5	15.5	16.5	16 0

Table II, and are plotted in Figs. 5 and 6. As was to have been expected, the pressure increases as the volume decreases. During a given period of heating the evolution of gaseous products of decomposition in "test with constant initial pressure," is constant. The equation

$$PV = K$$

where P is the pressure developed during a period, V the volume, and K a constant, holds for all volumes between 30 cc. and 60 cc. The av-

Fig. 6.

erage values of K are plotted in the curve shown in Fig. 7. This curve represents as nearly as may be, the course of the decomposition of a nitrocellulose when heated in a vacuum. In "test with increasing initial pressure" as the volume decreases the pressure increases according to a law which can be stated as follows: If the original volume be 60 cc., and if this volume be successively decreased by a constant quantity, then the pressure developed in one hour at any other volume can be found from the equation

$$P_n = P_{60} + \frac{n(n+1)}{2} C,$$

where P is the pressure expressed in millimeters of mercury, n the number of times the volume has been decreased by a constant quantity, and C a constant. For stable American collodion cotton P_{60} is about

43 mm. and, under the conditions above described, C is about 9. The above equation has been proven for volumes between 30 cc. and 60 cc.

The values of P_n, when plotted, give the rectangular hyperbola shown in Fig. 8.

A noteworthy feature of the curves showing the rate of increase of pressure developed by a nitrocellulose in "test with constant initial pressure" is that they are not straight lines nor smooth curves, but are made up of oblique and horizontal lines. This is discernible in the curves shown in Fig. 4 and is well marked in Fig. 7, wherein are plotted the average values of K, calculated from the data given in Table II. The step-like character of these curves reminds one of the curve representing the progress of the dehydration of a hydrated salt like $CuSO_4.5H_2O$, which can be transformed into lower hydrates, each having its own vapor pressure. The resemblance is sufficient to suggest the explanation that a given sample of nitrocellulose when heated at 140° has a characteristic decomposition pressure which is represented by the first approximately horizontal portion of the curve (A B, Fig. 7). As the heating progresses a new phase or component appears and adds its decomposition pressure or accelerative action to the previous one, giving the new horizontal section C D. The rate of increase of pressure represented by this part of the curve remains fairly constant until a new phase or component appears, whence results the horizontal section E F. It appears to be characteristic of nitrocellulose of good stability that the curves obtained in "test with constant initial pressure" have this step-like character plainly developed. In Fig. 9 the transition between two

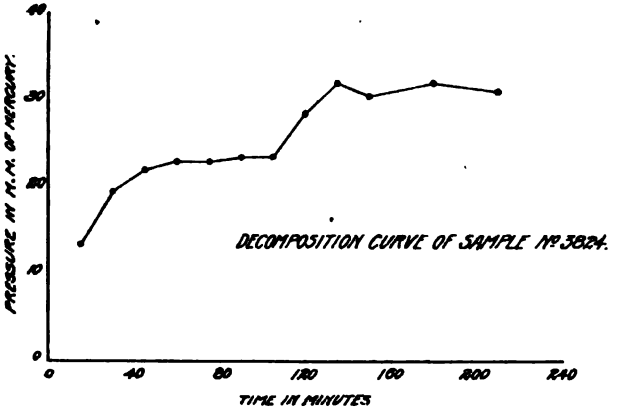


Fig. 9.

adjacent horizontal sections is well brought out. The curve shown in this figure was taken from the record of a different sample, No. 3222; in this case a fresh portion was taken for each pressure determination,

and the tube was kept evacuated until just before the period for which it was desired to measure the decomposition pressure of the material.

According to Saposhnikov[1] the relation of velocity of decomposition of a nitrocellulose to temperature for temperatures between 125° and 140°, and between 145° and 155° can be expressed by the equations $\left(\frac{dv}{dt}\right)$ max. $= 24.6 + 0.201t$ and $\left(\frac{dv}{dt}\right)$ max. $= 136.5 + 0.985t$, respectively; the ratio of reaction velocity to temperature within each of these ranges of temperature can therefore be represented by a straight line. Solving the two equations simultaneously, 143° is indicated as the temperature at which these two lines will intersect. At this temperature

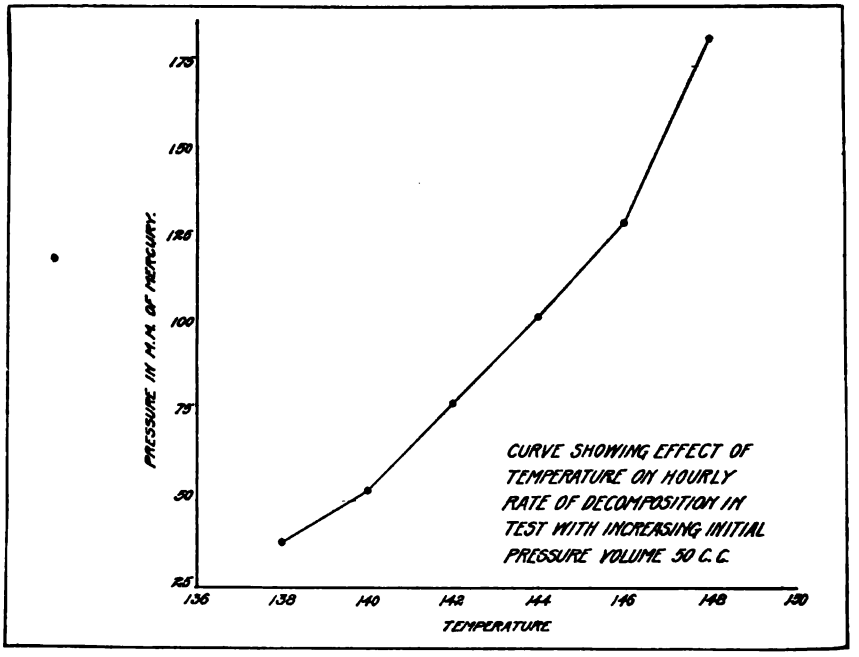


Fig. 10.

a sharp change in the ratio takes place in either direction. Before I became aware of Saposhnikov's work I had thoroughly studied the temperature relations of the Obermuller test, employing a temperature interval of 2° instead of 5°, as employed by Saposhnikov. My results between 138° and 148° are as follows (volume, 50 cc.):

Temperature:	138°	140°	142°	144°	146°	148°
Pressure (mm.)	38	53	77	103	130	183

From these data are obtained the curve shown in Fig. 10. Instead

[1] Russ. Phys. Chem. Soc., 38, 1186 (1906); reviewed by H. M. Gordin in Chemical Abstracts, May 20, 1907.

of one sharp change in the rate of decomposition at 143° there are here shown two such breaks, one at 140° and one at 146°. As the Obermuller apparatus uniformly gives concordant results within ±2 mm. the position of the curve is sensibly free from experimental error.

CHEMICAL LABORATORY,
SANDY HOOK PROVING GROUND.

[CONTRIBUTION FROM THE AGRICULTURAL CHEMICAL LABORATORY OF THE WISCONSIN EXPERIMENT STATION.]

VARIATIONS IN THE AMOUNT OF CASEIN IN COW'S MILK.

E. B. HART.

Received November 11, 1907.

There is a general belief among dairymen and some dairy chemists that casein and fat are present in milk in very constant relative proportions; that given the percentage of fat in milk, the percentage of casein can be directly calculated by rule. This rule was formulated by Van Slyke[1] and is based on averages of numerous analyses made at the New York Agricultural Experiment Station. The rule is to be applied especially to milks ranging from three to four and one-half per cent. of fat and is stated as follows: to find the per cent. of casein in milk when the per cent. of fat is known, subtract 3 from the per cent. of fat in milk, multiply the result by 0.4 and add the result to 2.1. The limitations placed on the rule as applicable to milks containing but from three to four and one-half per cent. of fat led the writer to inquire how applicable it might be to milks of higher fat content. Hill,[2] as early as 1890, showed that in individual cows the proportion between fat and casein is widely different. He, however, obscured this important fact by conclusions based on averages of many milk analyses. His conclusion was that normal milks, whether rich or poor, have on an average, one-fourth as much casein as total solids, though he further says that single samples may depart widely from this standard.

Shuttleworth,[3] from work on individual cows, showed that a considerable variation in the proportion of casein to fat existed among different animals, and that a ratio established for one period of lactation in any single animal may not be the same as the ratio found at some other period for the same animal.

A priori there seems to be no good reason why we should expect a definite quantitative relation between these two constituents of milk. They are entirely unlike in chemical constitution and their elaboration has been along different lines of synthesis. If we could suppose that they

[1] Modern Methods of Testing Milk," p. 192.
[2] Fourth Annual Rept. Vt. Agr. Exp. Sta.
[3] Rept. of Ontario Exp. Farm, 1895.

resulted from the splitting of a single chemical entity, then there l be reason for a definite relation between the amounts of these ubstances in this secretion. But the facts regarding the production lk constituents do not appear to support any such hypothesis. The variable milk constituent we have is the fat, which may rise and om day to day in no inconsiderable amount, dependent on feed and nvironment to which the animal is subjected. During such fluc- ons of the fat[1] content, the casein may remain constant. Instances n record where the fat content of the milk has dropped from 3.25 ent. to 2.20 per cent., while the casein content of those milks remained 08 and 2.18 per cent., respectively. This at least would indicate he precursor of these two important milk constituents was not a single ical entity, which seems a necessary assumption if the two substances o remain in constant relative proportion. On the other hand, it ates rather a differentiated process, with the formation of fat and 1 as distinctive and dependent upon inherent cell characteristics.

ain, the relation of fat to casein in the cow's milk established for eriod may not be found to be the same at some later period of lac- 1. In fact, it appears to be the normal tendency for the nitrogen ounds of milk to increase relatively to the fat with the advance of ion.

rther, while there is no doubt that the rule above formulated is accurate when applied to the mixed milk of herds made up of grade als, it appears entirely possible that it might not be applicable to l milk produced by animals of high fat-producing capacity.

The very fact that the efforts of progressive dairymen is to displace ow fat-producing animals with animals producing higher fat yields, introduce a tendency to move away from the application of the

om the standpoint of the breeder of dairy cows and the cheese in- y, it would appear extremely important to know whether or not als producing milks of five to six per cent. fat content, are produc- definitely related percentage of casein, and with animals producing to five per cent. of fat, whether that same relation holds true. If es not, then it would appear that here is important work for breed- f dairy cows in the selection and production of animals producing more fitted for the butter or the cheese industry, as the case may be.

dies of the University Herd.—No attempt was made to follow the al through long periods of lactation. The only attempt made here o learn whether the variations of fat to casein in different animals of any significance and what might be expected any time an analysis nade.

[1] Technical Bull. No. 1, N. Y. Agr. Exp. Station.

Casein determinations were made by the Official Agricultural Chemists' method. The only variation was the use of the factor 6.38 instead of 6.25. The samples were from a mixture of night's and morning's milk. Fats were run by the Babcock test from composite samples selected over a period of one week in the usual way. The collection of the samples for casein determination was made in the middle of the week during which the fat sample was being taken. The analyses cover a period from July 26th to August 7th. The data relating to the animals are arranged in the table according to breed. The table contains, besides the percentages of fat and casein, a column showing the amount of casein calculated by Van Slyke's rule from the fat content. Besides these data, two separate columns show the relations of fat to casein and casein to fat.

ANALYSES OF MILK OF UNIVERSITY HERD.

Breed.	No.	Per cent. of casein found.	Per cent. of casein calculated.	Per cent. of fat.	Relation of fat and casein.	Relation of casein and fat.
Jersey.....	1	2.45	2.60	4.27	1.74: 1	0.57: 1
	2	3.11	2.83	4.83	1.55: 1	0.64: 1
	3	3.31	3.28	5.95	1.79: 1	0.55: 1
	4	3.65	3.24	5.85	1.60: 1	0.62: 1
	5	3.00	2.81	4.79	1.59: 1	0.62: 1
	6	2.92	3.30	6.02	2.06: 1	0.48: 1
Guernsey.....	7	3.50	3.38	6.21	1.77: 1	0.56: 1
	8	2.77	3.30	6.01	2.16: 1	0.46: 1
	9	3.09	3.02	5.31	1.71: 1	0.58: 1
	10	3.12	3.08	5.46	1.75: 1	0.57: 1
	11	2.91	2.85	4.89	1.67: 1	0.59: 1
	12	2.60	2.94	5.11	1.96: 1	0.50: 1
	13	2.47	3.05	5.37	2.17: 1	0.46: 1
	14	2.98	3.31	6.04	2.03: 1	0.49: 1
Holstein.....	15	2.10	2.17	2.96	1.41: 1	0.70: 1
	16	2.13	2.17	3.19	1.49: 1	0.66: 1
	17	2.50	2.27	3.44	1.57: 1	0.72: 1
	18	2.16	2.32	3.56	1.55: 1	0.60: 1
	19	1.88	2.17	3.18	1.52: 1	0.65: 1
	20	2.15	2.11	3.03	1.40: 1	0.70: 1
Brown Swiss.....	21	2.66	2.61	4.29	1.61: 1	0.61: 1
	22	2.70	2.49	3.99	1.51: 1	0.66: 1
Ayrshire.....	23	2.56	2.34	3.61	1.41: 1	0.70: 1
	24	2.14	2.87	4.93	1.57: 1	0.63: 1
	25	2.47	2.28	3.47	1.40: 1	0.71: 1
	26	2.61	2.32	3.57	1.36: 1	0.73: 1

The table shows that in a large number of instances the application of the rule gives data agreeing closely with actual determination. There are, however, as Dr. Van Slyke has already emphasized, high fat milks where the agreement is not very close, and actual determinations would alone disclose their true casein content. No. 13, with a fat content in

the milk practically identical with that of No. 10, nevertheless shows a casein content 0.65 per cent. lower than the latter.

The table further shows that there is considerable variation not only among animals of different breeds, but between animals of the same breed. Percentage variation of casein ranges from 1.88 for Holsteins to 3.65 for Jerseys. Among Holsteins themselves the range of percentage is from 1.88 to 2.50, while among Jerseys it is from 2.45 to 3.65. Reduced to a ratio of pounds of fat to pounds of casein, we have among different breeds, for instance, at the time these analyses were made, No. 6, a Jersey, showing 2.06 pounds of fat for every pound of casein, while No. 17, a Holstein, shows 1.37 pounds of fat for one pound of casein. No. 8, a Guernsey, shows 2.16 pounds of fat for every pound of casein, while No. 25, an Ayrshire, shows 1.4 pounds of fat for one pound of casein. These are the extreme cases among the number of animals investigated.

Among breeds themselves, we have No. 6, a Jersey, with a ratio of 2.06 punds of fat to 1 of casein, while No. 3 of the same breed shows a ratio of 1.79 pounds of fat to every pound of casein. Stated in another way, No. 6 shows 0.48 pound of casein for 1 of fat, while No. 3 shows 0.55 pound. The data on the milks of these two cows clearly shows that relative to their fat, No. 3 is the greater casein producer. The yield of cheese from the milk of No. 3 must necessarily be larger, under uniform conditions of manufacture, than from that of the other animal. Again, No. 7 showed a relation of 1.77 pounds of fat to 1 of casein, while No. 8 showed the relation of 2.16 to 1. No. 7 shows the relation of casein to fat as 0.56 to 1, while No. 8's relation is 0.46 to 1. The milks from these animals were at about the same period of lactation.

A further consideration of the table reveals the fact that among breeds the Holsteins, Brown Swiss and Ayrshire uniformly show a higher relative proportion of casein to fat than do the Jerseys and Guernseys. It also shows that certain individuals among the two latter breeds may show as high a relation of casein to fat as certain individuals among the other breeds.

What these animals will do for a whole year is not known, but enough data is at hand to emphasize the fact that individual differences in casein-producing power do occur among animals of different breeds, and surely may occur among animals of the same breed, and that the casein-producing power does not necessarily bear any close relation to the fat-producing power. That a higher fat holding milk means an increased casein holding milk is not here denied, but that the increase is in a fixed proportionate ratio, the data do not support. It emphasizes, it seems, the fact, that the casein-producing function is in part, if not largely, individualistic, and capable of being used in producing dairy types of animals, either for an industry in which fat plays the most important

rôle, or for a cheese industry, where both fat and casein are primarily concerned.

Summary.

1. The relation of casein to fat in cow's milk is a variable one.
2. One of the prime factors controlling its relation is individuality.
3. The relation of casein to fat varies among animals of different breeds and among animals of the same breed.
4. Direct determination of both fat and casein seems necessary in determining the value of the milk of any single cow for cheese production.

NOTES.

The Use of the Centrifuge.—Attention has recently been called to the advantage of the laboratory use of centrifugal action for separating crystals from their mother-liquor—a process which has long been of great service in technical operations on a large scale.[1] The object of this note is to point out certain important precautions necessary in the use of this highly serviceable apparatus. The word of caution seems to be especially demanded because new apparatus is being put upon the market by several firms, and the novice may be unfamiliar with the intensity of the centrifugal effect, and the consequent danger inherent in improperly constructed machinery.

It is well known that the forces acting to drain out the liquid in a centrifuge are $\frac{4\pi^2n^2r}{g}$ times as great as they would be in a gravity-vat with a perforated bottom, if n = the number of revolutions per second, r the radius, and $g = 980.6$. Thus if $n = 20$ (*i. e.*, 1200 revolutions per minute) and the radius of the centrifuge is 10 centimeters, the drying is nearly 160 times as great as that effected by gravity—a very great advantage. It must not be forgotten, however, that the strain upon the apparatus increases in the same proportion, being quadrupled for each doubling of the speed. Therefore with high speeds great strength is necessary. Even great steel fly-wheels sometimes burst under their strain. For this reason, centrifugal apparatus constructed of fragile material should never be run rapidly, and even with the simplest and strongest apparatus, the machine should *always be surrounded by a very strong casing or box of wood or metal*, so that no harm would result if anything should break. For the same reason rapidly revolving centrifugal apparatus should *never be constructed of glass, unless the glass is enclosed in metal in such a way that the fragments will not fly if broken.* Glass apparatus is frequently not well annealed, and is liable to break under the heavy strain.

[1] Richards, This Journal, 27, 104 (1905); Ber., 40, 2771 (1907). Köthner, Chem. Ztg., 1907 (No. 73).

At Harvard the funnel-centrifuge, alluded to by Köthner, is made of ıtinum, but porcelain funnels and receivers may be used without dan- r if the rate of revolution is not too great. I have never dared to e glass funnels in this apparatus. The porcelain basket-centrifuges, which several forms are on the market, will stand considerable strain; e speed at which they may safely run varies with the form and stout- ss, and should be carefully determined for different loads and indicated · the manufacturer. The porcelain receiver surrounding them is never ·ong enough to hold the fragments if the basket should break; there- ·e this whole apparatus also should be surrounded by a strong guard- x. Both porcelain and glass should be supported on some kind of rub- r cushion, so as to distribute the strain as evenly as possible.

It is not out of place to call attention to another somewhat less se- ıus but nevertheless important precaution, namely, the equal distri- tion of the load. This is essential if the apparatus is to run smoothly d the strain is to be evenly distributed. In the case of the funnel- ıtrifuge the adjustment is very readily accomplished by hanging the posite funnels upon the two arms of a common balance, and filling em to equilibrium with similar crystals about equally moist. In the se of the basket-centrifuge, the distribution must be made with a atula, before the machine is started.

If these simple and obvious precautions are taken, the centrifuge ll be found, as has been said before, a very valuable aid in the puri- ation of small quantities of substance in the laboratory of the inves- ;ator. In the course of twenty years no serious accident has resulted ım its use at Harvard, and much has been gained. As has been said fore, the gain to be expected varies greatly in different cases; it is :atest in the case of very soluble substances which do not carry im- rities in isomorphous solid solution with them into the solid state, d least in the case of slightly soluble substances, which contain isomor- ous contamination.

To summarize the contents of this brief note—the value of centrifu- l action in purifying substances has been once more emphasized, t the importance of equal distribution of the load, the danger of using ıss or other very fragile material in the centrifuge, and the necessity caution in regulating the speed and in always guarding the operator a stout casing around the machine, is pointed out.

T. W. RICHARDS.

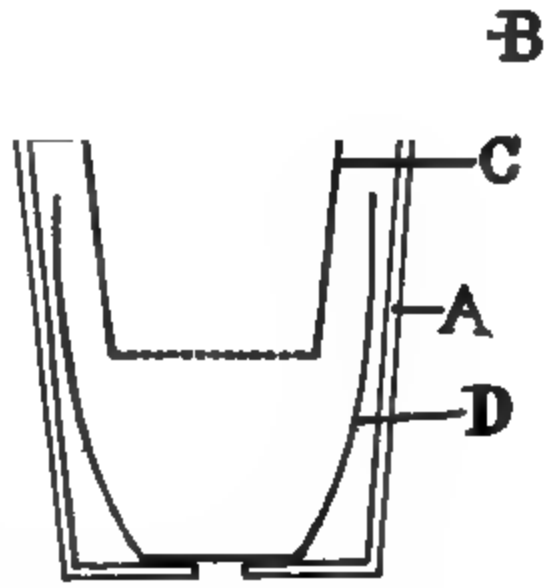
HARVARD UNIVERSITY,
November 25, 1907.

Apparatus for the Centrifugal Drainage of Small Quantities of Crys- s.—The high efficiency and importance of centrifugal drainage in : removal of mother liquor in purification by crystallization has re-

cently been strongly emphasized by T. W. Richards,[1] who describes various convenient forms of apparatus for the purpose. The use of these devices in this laboratory has led to the construction of a new very convenient modification of centrifuge which not only makes possible the complete removal of mother liquor from small quantities of substance without undue loss of material and in a cleanly fashion, but also provides for the preservation of the mother liquor and rinsings from the crystals in an equally satisfactory manner. This latter point is frequently of importance to any chemist who is purifying small quantities of precious material, especially if the substance is very soluble.

The following diagram explains the construction of the device, which has already been briefly described:[2]

A is a cup, preferably of aluminum on account of its lightness and cleanliness, with trunnions by means of which it may be hung upon one end upon of a metallic arm attached to the head of a centrifugal machine. A similar cup, suitably weighted, serves as a convenient counterpoise. These cups are of the form commonly employed to contain the flasks used in the determination of fat in milk.[3] A hard rubber sleeve *B* fits loosely upon the top of the aluminum cup, the inside of the sleeve being turned to the proper size and angle to hold a platinum Gooch crucible *C*, of any desired size, which serves as the basket for the crystals. Sleeves of metal, platinum plated, might be used, but are objectionable on account of their weight. With a low-speed centrifuge, a porcelain Gooch crucible would probably be safe. For obvious reasons the top of the crucible should extend a few millimeters above the sleeve. The mother liquor drains into a platinum crucible *D*. Where platinum is unnecessary for the sake of purity of the mother liquor, the crucible *D* may be replaced by a suitable stout glass vessel. Thin beakers, however, are likely to be fractured by the weight of the liquid, if the speed of revolution is high. Although the surface of the aluminum cup may easily be kept bright and shows no tendency to abrade and thus contaminate the mother liquor, all possible danger from this source may be avoided by lining the inside of the cup with a cylinder of platinum



[1] This Journal, 27, 210 (1905).

[2] Baxter and Coffin, *Ibid.*, 28, 1582 (1906).

[3] Aluminum cups of this sort are made by the International Instrument Co., Cambridge, Mass.

turned over the upper edge of the cup. The latter precaution is course more necessary when acid vapors are emitted by crystals or ther liquor. The Gooch crucible, or the whole top of the cup, may covered with a circular piece of platinum foil, the edges of which have n turned down to hold it in place. A hole in the bottom of the alumi- n cup facilitates the removal of the vessel containing the mother ior.

t is, of course, possible to make the apparatus more elaborate, for ance, by providing the aluminum cup with an especial porcelain platinum lining. The system as described above, however, has the at advantage that it may be constructed with materials available most laboratories.

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CAMBRIDGE, MASS.,
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REVIEW.

RECENT PROGRESS IN PHYSICAL CHEMISTRY.

F. G. COTTRELL.

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'he issuance by our Society this year of "Chemical Abstracts" has ıewhat changed the requirements for the annual reviews of special ics. Heretofore their chief aim has been to present a brief synopsis the more important foreign literature, to supplement the "Review of ıerican Chemical Research" included in the monthly numbers of the rnal. Since, as far as collection of data is concerned, all of this field is v covered by the "Abstracts," the author has, in what follows, con- d himself to the discussion of a few selected topics which have either racted special attention of late or seem to open up or emphasize new or viously neglected fields of inquiry. In order to present some of these heir true perspective it has seemed necessary to trace the same line of ught back among the earlier workers, and in this respect there has been attempt to limit the present article strictly to what has appeared dur- the past twelvemonth. As heretofore, the subject of radioactivity been left for treatment in a separate article.

'erhaps the most significant trend of recent work is to be found in the ıcentration of effort toward narrowing the gap between molecular and lar phenomena. This field in which, among other important matters, whole subject of colloids ultimately belongs, stands to-day in very ch the same relation to physical chemistry and ordinary mechanics t physical chemistry stood to physics and chemistry twenty or thirty rs ago. The classification of natural phenomena into sharply defined ıjects may in most cases be interpreted simply as an admission that we omitting a region between, in which, as we enter it from either side, methods of treatment gradually fail us. Thus it was that the trouble- ne and outgrown distinction between chemical and physical combina- n was swept away by Gibbs, and under the broader conception of hase" and "component" the two fields merged in one as far as hetero-

geneous equilibrium was concerned; but here Gibbs' definite contribution ended. The very conception of a "phase" in whatever words it is defined rests eventually upon the distinction between molecular and molar magnitudes. To emphasize this point of view we may frankly define a phase in the sense in which Gibbs uses the term, as a portion of matter homogeneous down to molecular magnitudes.

This gives us a perfectly sharp classification of systems until we reach the colloids. Then classification by its means ceases to be independent of theoretical assumptions, and depends upon where we arbitrarily draw the line between molecular and molar magnitudes in a series which passes through all possible values intermediate between the typical unquestioned extremes. It is this characteristic of a boundary or frontier region which has lent the subject of colloids much of its fascination for the investigator. Many, apparently overlooking the necessity that colloid phenomena must eventually furnish the connecting link between molar and molecular types, have striven to build up a new and entirely independent science on this foundation. This tendency has undoubtedly been greatly stimulated by the importance of colloids in biological problems. Where we may hope for the greatest permanent advances is, however, in the extension, with the necessary modification, of the well established notions from over both its border lines into the new field until they meet and merge in one more generalized set covering the whole extent. When, for instance, we are able to trace the phenomena of osmotic pressure up through the solutions of substances of large molecular weight such as the starches and simpler proteins on to the inorganic colloids and finally connect it with its equivalent in the unquestioned suspensions, we will have done much to realize Newton's dream of laws broad enough to embrace both chemistry and astronomy, stellar and atomic mechanics. Several recent papers in this direction deserve particular notice. Einstein (A. Einstein, *Ann. Physik* [4], **17**, 549–60 (1906); **19**, 289–306 (1906); **22**, 569–72 (1907)); with the aid of the molecular kinetic theory has developed the laws for "the osmotic pressure of suspended particles," also the "viscosity of a liquid holding in suspension a multitude of rigid spheres." The law of this generalized osmotic pressure, as we might style it, proves to be identical with that we have long been familar with in purely molecular phenomena, while the change in the apparent coefficient of viscosity of a liquid produced by the introduction of suspended particles is shown to be equal to the ratio of their total volume to that of the liquid, at least for small values of this ratio where the suspended particles are large compared with the molecules of the liquid.

From these two relations he then proceeds to calculate the rate of diffusion, in terms of the size of the particles and by comparing the results thus obtained with the values of molecular dimensions derived from other sources and the known diffusion coefficients of true solutions, shows the new formulae to agree with our present conceptions in those regions where the two overlap. A few of the most important formulae derived by Einstein, and the values of the symbols used are as follows:

(1) $P = \frac{RT}{V}\frac{n}{N}$

(2) $\frac{K'}{K} = 1 + \phi$

(3) $D = \frac{RT}{N} \cdot \frac{1}{6\pi K r}$

(4) $\lambda = \sqrt{2Dt} = \sqrt{\frac{RTt}{3N\pi K r}}$

$$(5)\ Nr^3 = \frac{3}{4\pi c}\left(\frac{K'}{K} - 1\right) \qquad (6)\ Nr = \frac{RT}{6\pi K}\cdot\frac{1}{D}$$

P, V, R and T have the usual signification as in the gas laws.
N = number of molecules in a gram molecule.
n = number of suspended particles in volume V.
r = radius of suspended particles.
D = diffusion constant of suspended particles.
K = specific viscosity of pure liquid.
K′ = specific viscosity of liquid with suspended particles.
ϕ = combined volume of suspended particles in unit volume of the liquid.
π = ratio of circumference to diameter of circle.
λ = mean displacement of a particle in a particular direction during time t.
c = molecular concentration of dissolved substance.

Perhaps it is only fair to point out that the weakest point in these papers as a whole lies in the author's tacit assumption in the original development that the suspended particles are large as compared with the structure of the liquid and then in subsequently applying the formulae to cases of typical solutions such as sugar in water where the question might be raised whether the sugar molecule in solution were large enough in comparison to the water molecule to justify this procedure. The author's determination of ϕ by equation (2) for a 1 per cent. sugar solution leads to a value four times that of the solid sugar, which he explains by each sugar molecule carrying an envelope of over 30 water molecules with it. These possible objections however lose significance entirely when we turn to suspended particles of relatively large dimensions, which are, after all, of chief interest to us in the present connection. Einstein suggests in passing that this opens the way to settling the disputed question as to the origin of the Brownian movements. What makes this work of particular significance at present is the surprising manner in which its predictions have been met by entirely independent experimental evidence from another quarter.

It is some years since Siedentopf and Zsigmondy brought out their "ultramiscroscope" which is simply an application to the study of excessively minute objects under the miscroscope, of a principle which has long been familiar to us in viewing excessively distant objects in the telescope; *viz.*, that an object which subtends thousands of times too small a visual angle to have its outlines seen, becomes visible as a point of light when strongly illuminated and viewed against a dark background, provided that the distance between such points is still perceptible in the ordinary sense. Thus by powerfully illuminating a submiscroscopic suspension of particles by a beam of light at right angles to the line of sight, we are able to perceive the position of each particle, although its shape is not merely far beyond our power of vision, but also beyond the theoretical limits of the miscroscope, which are set by the wave length of light itself. The relative sizes of the particles may be estimated roughly from their apparent brightness. The limits of ordinary miscroscopic vision may fairly be set at about 0.00025 mm. (*i. e.*, 250 $\mu\mu$) while the ultramiscroscope extends the limit of perception down to particles about 6 or 7 $\mu\mu$ in diameter. The closeness with which this approaches ordinary

molecular dimensions may be judged by comparison with the values derived from the molecular kinetic theory. Thus Loby de Bruyn sets the diameter of molecules of soluble starch at 5 $\mu\mu$, Jäger those of chloroform at 0.8 $\mu\mu$ and O. E. Meyer the water molecule at 0.1 $\mu\mu$. A most excellent and conservative view of the progress made in this subject up to about two years ago is to be found in Zsigmondy's own book. (Zur Erkenntnis der Kolloide; R. Zsigmondy, Jena (1905), G. Fischer 186 pp.). Much valuable work has since appeared along the same lines, but we can consider here only one of the most recent developments which bears directly upon the theoretical matters pointed out above.

Svedberg (T. Svedberg, *Z. Elektrochem.*, **12**, 853–60, 909–10 (1906)) in working out the technique of the above method has devised a very ingenious scheme for observing and measuring the amplitude and period of vibration of colloid particles, and has applied this to the study of colloidal solutions of a number of metals including sodium, potassium and calcium in various organic solvents, the method of preparation of the alkali metal colloids being also due to Svedberg himself (T. Svedberg, *Ber.*, **38**, 3616–20 (1905); **39**, 1705–14 (1906)). The mode of operating consists essentially in allowing the colloid solution to flow through the field of the ultramiscroscope at a known speed. The motion of each individual particle due to the flow, compounded with that component of its vibratory motion at right angles to both this and the optical axis of the miscroscope produces a path closely resembling a sine curve which is traced so rapidly by the luminous point that it appears as a continuous line of light which allows of its dimensions being estimated with fair accuracy on an eye-piece micrometer. Svedberg finds that for particles of equal size and character in different liquids, the product of amplitude into the coefficient of viscosity of the liquid is a constant as required by Einstein's formula. The numerical value of the constants as derived from the observations is about six times that computed from Einstein's formula, but remembering that the theoretical formula contains two very uncertain quantities—diameter of the particle and number of molecules in a gram molecule—the agreement is astonishingly close, more especially as Svedberg's experimental data were published without knowledge of Einstein's work, only his last paper above referred to taking cognizance of the latter. What lends this kind of work special interest at present is the growing deadlock between what we may call the extreme thermodynamic school including such men as Mach and Ostwald on the one side and the extreme mechanists such as J. J. Thomson, Rutherford and Arrhenius on the other. The question is as to which represents the more fundamental conception of natural laws. Each form of treatment is applicable to the whole range of molar phenomena. It is only in case we come to deal experimentally with individual molecules that a choice between them becomes anything more than a matter of philosophic taste. If we do come to deal with individual molecules in the sense of the kinetic theory, Maxwell's Demon will have been realized and the limits of applicability of the second law of thermodynamics exceeded, and the old quest for perpetual motion of the second type once more reinstated among serious scientific pursuits. On the other hand, if thermodynamics, as far as the second law is concerned, succeeds throughout in its application to indefinitely small portions of matter, then the molec-

ar theory, in its present form at least, must be given up as an objective onception of nature.

In this connection a remark of Ostwald's (*Z. physik. Chem.*, **57**, 383 907)) in reviewing Zsigmondy's book is significant as showing the fect that such recent work is having on even the most extreme repre-ntatives of the non-mechanistic school. He says "Von den vielen igentümlichkeiten sei in erster Linie die merkwürdige Eigenbewegung er submikroskopischen Teilchen erwähnt, die an die Brownsche ewegung erinnert, aber von ihr verschieden ist. Der Berichterstatter uss bekennen, dass er noch nicht absehen kann, wie diese ausser Zweifel ehenden Tatsachen sich ungezwungen mit dem zweiten Hauptsatze erden vereinigen lassen. Hier scheinen Maxwell's Dämonen, die man n molekularen Gebiete als ungefährlich ansehen durfte, im Endlichen, Sichtbaren ein freies Feld für ihre experimentelle Widerlegung des weiten Hauptsatzes zu haben." Svedberg has more recently (T. Sved-erg, *Z. physik. Chem.*, **59**, 451–8 (1907)) contributed another article iggesting certain hypothetical mechanisms violating the second law.

It is probable that the wonderful success which mechanistic methods ave met with in the field of radioactivity has had much to do with rengthening their position of late among chemists. To follow out this ne would carry us too far afield, but it may be pointed out in passing iat owing to the extreme delicacy of the methods of measurement the adioactive phenomena offer a promising field for the study of individual, tomic, and molecular phenomena, as illustrated for example in the pinthariscope and yet more quantitatively even in a recent paper by ohlrausch (F. K. W. Kohlrausch, *Sitzb. Akad. Wiss. Wien.*, **115** [2a], 73–82 (1906); *Physik.-chem. Centr.*, **4**, 219) upon variations in the rate of adioactive change from the mean value.

Turning now from the progress made along molecular kinetic lines to the ibject of thermodynamics proper, we meet a set of no less important dvances from the chemist's standpoint. These run back genetically or several years and include contributions from a number of well-known orkers, chief among whom may be mentioned, somewhat in chronological rder, the names of: Lewis (*Proc. Am. Acad. Arts and Sci.*, **35**, -38 (1899); **36**, 145–68 (1900); also *Z. physik. Chem.*, **32**, 364–400; **5**, 343–68), Richards (*Proc. Am. Acad. Arts and Sci.*, **37**, 1–17 (1901); **7**, 399–411 (1902); **38**, 293–317 (1902)), Tammann (Krystallisieren und chmelzen (1903) espec., p. 42), van't Hoff (Boltzmann Testschrift, p. 233–41 1904)), Trevor (*J. Physic. Chem.*, **9**, 269–310 (1905)), Bell (*J. Physic. hem.*, **9**, 381–91 (1905)), Haber (Thermodynamik technischer Gasreak-onen (Münich, 1905)), the whole as viewed at present seeming to have ilminated in a most remarkable paper by Nernst (*Nachr. Ges. Wiss., öttingen* (**1906**), [1], 1–40), published early last year and since rought more directly before American chemists by the Silliman lectures 'Experimental and Theoretical Applications of Thermodynamics to hemistry," Chas. Scribner's Sons, New York, 1907, 123 pp.) given by rofessor Nernst in New Haven, and of which it formed the basis.

It represents what promises to be the most important contribution of iermodynamics to chemistry since the work of Gibbs and Helmholtz, nd forms a fine example of the magnificent results which the pure ther-iodynamical method is capable of accomplishing within its most fruitful eld of application. The presentation in the original is already so com-

pact and derives its individual steps from such diverse sources that it is impossible to give comprehensively even an outline of it here. (See Abstract by Abegg, *Z. Elektrochem.*, **12**, 738–43 (1906)). In as far as the outcome of such a thorough-going and detailed contribution as this can be reduced to epigrammatic statement we might perhaps say that it represents the amplification and correction of the old "law of maximum work" so as to cover changes in heat capacity and concentration in the reacting system, it being recognized that the disregard of these factors was what most seriously limited the applicability of the law as first advanced. Nernst points out that in its original form the law was true for all systems at absolute zero and very near the truth at higher temperatures for many changes involving only pure solids and liquids or at best concentrated solutions. He then introduces as his fundamental hypothesis the proposition that not only are the free and total energy of any system equal at absolute zero but their first derivatives with respect to temperature are also equal at this point. This necessitates specific heat being a strictly additive property at absolute zero and consequently the variation in heat of reaction with temperature depends solely on the temperature coefficient of specific heat. Starting now with the well-known van't Hoff equation for equilibrium

$$Q = RT^2 \frac{d \ln K}{dT},$$

assuming in the neighborhood of absolute zero a difference of 3.5 cal. between the molecular heat of the vapor at constant pressure and that of its corresponding solid or liquid, he deduces the working equation

$$\log K = -\frac{Q_0}{4.571T} + \Sigma\nu 1.75 \log T + \frac{\Sigma\nu\beta}{4.571} T + \Sigma\nu C$$

Q_0 = heat of reaction for T = 0.

ν = number of molecules of each species counted positive on one side of equation and negative on the other.

β = temperature coefficient of atomic heats.

C = specific "chemical constant" for each molecular species.

The additive nature of these "chemical constants" is perhaps the most significant result of Nernst's development. This permits us to predict the true chemical equilibrium in any system from the heat of reaction and certain purely physical constants of the individual substances originally brought together, and since the purely physical phenomena of vaporization is merely a special case of equilibrium, the numerical value of C for each substance may be derived from a study of the temperature-vapor pressure curve for that pure substance. By a skilful use of a modified law of corresponding states, Nernst has even gone further and made it possible to calculate this constant C if we have an approximate value for the critical pressure of the substance and in addition know for some one temperature: (1) the vapor pressure, (2), the heat of vaporization, (3) the temperature coefficient of the latter. The value of these "chemical constants" seems to vary between relatively narrow limits. Of the twenty-three examples given, the lowest is hydrogen, 2.2 and the highest alcohol, 4.1. They rise fairly regularly with the boiling-point in the case of simple substances but are abnormally high in the case of polymerizing substances. For the application of the equation to actual cases, including

a discussion of permissible simplifying assumptions, the original must be consulted. (See also K. G. Falk, THIS JOURNAL, **29**, 683–87 (1907)). Among the interesting consequences of the theory may be mentioned the deduction of a more exact form for Trouton's rule including a logarithmetric term, and the treatment of the question of the stability of chemical compounds from a perfectly general standpoint. This latter aspect has been developed at some length by Brill (*Z. physik. Chem.*, **57**, 721–38 (1907)) both for homogeneous and heterogeneous systems. For the case of a gaseous compound, each of whose molecules dissociates forming two new molecules, as, for example N_2O_4 into $2NO_2$, he deduces for a pressure of one atmosphere, the following table of approximate temperature (T) on the absolute scale, at which the dissociation will be one-half complete for reactions with a given heat of reaction (Q) at constant pressure and ordinary temperature, irrespective of the specific character of the substances involved.

Q.	T (absolute).
10,000 cal.	290°
15,000	405
20,000	525
30,000	780
50,000	1220
100,000	2350
200,000	4500

Leaving the subject of energetics and passing on to the properties of matter, we must place in the forefront Landolt's paper (H. Landolt, *Sitzb Akad. Wiss. Berl.*, **8**, 262–98 (1906); *Z. physik. Chem.*, **55**, 589–621 (1906)) on the change in total weight during chemical reaction. This paper represents the result of years of patient work (H. Landolt, *Z. physik. Chem.*, **12**, 1–34 (1893)) in what to many must have appeared a hopeless, not to say thankless, cause. Step by step the accuracy of the experiments were increased until the probable error of a complete experiment had been forced down to so small a fraction of the minute changes which Landolt was here in search of, that he could be positive of the existence of new phenomena which all our work since Lavoisier had demonstrated to be undetectable. To summarize the actual results it may be said that out of the 14 reactions of various types studied, only two gave systematically a change in weight decidedly larger than the errors of observation. These were the reductions of silver sulphate or nitrate by ferrous sulphate and the reduction of iodic acid with hydriodic acid. The experiment involved a mass of reacting material of about 250–350 grams, the total experimental error determined from blank control experiments not exceeding 0.03 mg. Every one of nine separate experiments on each of the above reactions gave a loss in weight which ranged in the first reaction from 0.068 mg. to 0.119 mg. and in the second reaction from 0.047 to 0.177 mg. Out of the 75 experiments performed in all, 61 showed loss in weight and the greatest gain in weight in any experiment was 0.019 mg. or well within experimental error. From the data thus far obtained it does not seem possible to connect the type of reaction with the sign or magnitude of the changes in weight. In the paper the possibility is suggested that the loss in weight merely represents the escape of electrons. Landolt's transfer from the University

to the Reichsanstalt temporarily interrupted this work but it is now reported that he has it actively under way again.

The relation of chemical constitution to crystal structures, although almost of necessity a close one, has been one of the least productive fields of inquiry either for the experimenter or the theorist. We have, to be sure, made some progress in the limited field where we have had the rotation of the plane of polarized light to help us, but this merely scratches the surface of the general problem, and leaves the most fundamental geometrical aspects of the question as obscure as ever. It is with all the more satisfaction, therefore, that we welcome the recent attempt of Pope and Barlow (*J. Chem. Soc.*, **89**, 1675–1744 (1906); *C. A.*, **1907**, 1809; see also Review in *Am. Chem. J.*, **37**, 638–54) to indicate a line of attack for this problem which really reaches the basic geometric principles in a perfectly concrete manner. The greatest stumbling block at the very outset has been the erratic way in which series of related compounds are distributed among the various crystallographic systems or classes of symmetry. Tutton's classic work (see *J. Chem. Soc.*, for past ten years) on isomorphic salt series has given us a fairly clear idea of the relations existing within these latter series. The present paper on the other hand derives much of its strength from its method being essentially independent of the distinction between even the crystal systems or classes of symmetry, the system of reference adopted being a modification of the topic axis idea in which the sum of the valencies of all atoms in the compound takes the place of the specific volume heretofore used in defining these axes. The physical hypotheses upon which the whole development is based are: (1) that crystal structure is determined by the arrangement of the atoms, or better their spheres of influence, in such wise as to present the closest possible packing of the assemblage and (2) that the volumes of the spheres of influence of the different atoms in a compound are directly proportional to the valencies of the atoms. Starting with these simple arbitrary hypotheses it is surprising what a vast mass of heretofore apparently unrelated chemical and crystallographic facts the authors are able to coördinate and explain. As many of them are cited in the abstract above referred to they need not be repeated here. It is interesting and suggestive to compare this theory of valence, derived as it is primarily from the crystallographic standpoint, with that of Abegg and Bodlander which had its origin in electrochemical phenomena and the closely related theory of Werner (see last year's review THIS JOURNAL, **27**, 908, also A. Werner, *Ber.*, **40**, 15–69 (1907)) which was purely chemical in origin. Perhaps the most fundamental difference between the present theory and its predecessors is its freedom from any assumption of intrisic polarity within the atoms themselves, the definite assignment of which forms so important a part in Abegg's scheme. Pope's conception of valence leads here to the admission that the valencies of different atoms need not necessarily bear exactly the simple ratio to one another that we are accustomed to assign. There is, to be sure, nothing in pure chemistry to contradict this, but such a condition of affairs would be hard to reconcile with Faraday's laws of electrochemical equivalents.

Traube, also (J. Traube, *Ber.*, **40**, 137–39 and 723–33 (1907)), has recently attempted to refer valence to atomic volume, basing his deduction, however, on the refractive index of isotropic substances with the aid of the electron theory and a number of rather specialized assumptions

as to the division of the atomic volume among the essential parts of what may be termed the atom as a whole. Still another radically different view of valence based on an assumed eccentricity of the atomic nucleus in its ether envelope is presented by Ensrud (G. Ensrud, *Z. physik. Chem.*, **58**, 257–87 (1907)) and supported by evidence drawn from the specific heat of gases. Thus far our theories of valence have for the most part dealt only with the building up of atoms into molecules but the time seems fast approaching when they must also be made to connect with the theories concerning the structure of the atom itself which the study of radioactivity and related topics are fast forcing upon us. On the whole, the subject of valence seems to present just at present an exceptionally promising field for the chemist who can without prejudice freely correlate the partial truth evidently contained in each of the above rather specialized treatments of the general subject. We may, in passing, refer to a historical sketch of the conception of valence recently published by Herz (*Chem.-Ztg.*, **30**, 1273–5 and 1284–6 (1906)).

The subject of liquid crystals still continues to attract much interest, but thus far the work has been chiefly from the preparative side. Vorländer (D. Vorländer, *Z. physik. Chem.*, **57**, 357–64 (1907)) has described a number of very interesting and beautiful examples, chiefly azo compounds, which show not only one but two liquid crystal modifications and some which remain in the crystalline state over more than a hundred degrees of temperature. Under certain conditions he states that it is possible to obtain liquid crystals with well defined angles and straight edges. Lehmann (O. Lehmann, *Z. physik. Chem.*, **56**, 750–66 (1906), and Jaeger (F. M. Jaeger, *Rec. trav. chim.*, **25**, 334–51 (1906), and *Versl. Akad. Wet. Amsterdam*, **15**, 345–8; 389–401; 401–10 (1906)) have described a long series of esters of cholesterol and phytosterol, all of which show anisotropic liquid forms. According to Lehmann, every one of the cholesterol esters may be had in two anisotropic liquid forms although in most cases, one of these is labile while Jaeger claims a total of five possible, distinct, liquid phases, for the cinnamic acid ester. Double bonds and the presence of certain groups, such as the azo and azoxy, seem to favor greatly the appearance of these very soft crystals, which indeed is what they really are. What may seriously be called quantitative physical measurements on these crystals, have as yet scarcely been undertaken, but with the rapidly increasing list of substances now at our command to draw from, the opportunities here presented for fundamental work, the direct comparison of crystal building forces with surface tension and ordinary mechanical stresses, cannot long remain unappreciated by investigators. Merely by way of suggestive example may here be cited the work of Lehmann (O. Lehmann, *Ann. Physik*, **21**, 381–3 (1906)) on the relative orientation of the two forms of crystal as they pass over into each other at the transition point; also the fact that fluid crystals on glass surfaces seem always to orient themselves with their optic axes as nearly perpendicular to these surfaces as possible. Silver iodide seems to be practically the only typical electrolyte which has been shown to possess an appreciably fluid anisotropic form. Kohlrausch (W. Kohlrausch, *Wied. Ann.*, **17**, 642 (1882)) long ago showed that the electrolytic conductivity of this substance undergoes a tremendous change in passing from the hard to the soft crystalline state at 145°, but that the change from the soft or liquid crystal state to

that of an isotropic liquid occasions scarcely a perceptible break in the temperature-conductivity curve. This, in the light of our present conception of liquid crystals, brings us face to face with the question of the degree of electrolytic dissociation in crystals of strong electrolytes. Lorenz (R. Lorenz, "Elektrolyze Geschmolzener Salze," Bd. III 297–311; *Monogr. über angew. Elektrochem.*, Bd. 22, Halle (1906)) has come out flatly in favor of the assumption of a high degree of electrolytic dissociation in solid crystalline salts, attributing their low conductivity in the solid state almost exclusively to the high internal friction. Much work has been done on metallic conductivity in different directions through the crystal, but a corresponding study in a thorough and systematic manner for electrolytic conductivity is still lacking, and although presenting many difficulties it promises very interesting results (Tegetmeier, *Wied. Ann.*, **41**, 18 (1890)).

The study of electrolytic dissociation in non-aqueous solutions has received its most important contributions of late from Walden in a continuation of the work already reported in last year's review (THIS JOURNAL, **28**, 905 (1906)). Nine articles in this series have now appeared, *viz*: I, General Introduction (P. Walden, *Z. physik. Chem.*, **46**, 103–88 (1903)); II, Electrical Conductivity (*Ibid*, **54**, 129–230 (1905)); III, Viscosity and its Relation to Conductivity (*Ibid.*, **55**, 207–49 (1906)); IV, Molecular Weight by Boiling-Point Method (*Ibid.*, **55**, 281–302 (1906)); V, Solubility (*Ibid.*, **55**, 683–720 (1906)); VI, Heat of Solution (*Ibid.*, **58**, 479–511 (1907)); VII, Heat of Dissociation and Heat of Solution (*Ibid.*, **59**, 192–211 (1907)); VIII, Relations of Refractive Index and Electrolytic Dissociation (*Ibid.*, **59**, 385–415 (1907)); IX, Electrostriction (*Ibid.*, **60**, 87–100 (1907)). One of the most salient features of the work is the sharpness with which Walden has been able to separate the effects of changes in the degree of ionization from those due to the friction of the moving ions. The key to Walden's success is to be found in his systematic plan of campaign. He first worked over in a qualitative way a very wide range both of solvents and solutes and from these selected a working list of about fifty typical solvents and some four or five solutes. The strictly quantitative work was then chiefly confined to these substances and their mixtures. The solutes were for the most part iodides of organic ammonias, the most complete series of measurements being carried out upon solutions of tetraethyl ammonium iodide. The first important outcome of the work, as already noted in last year's review, was the giving of a quantitative form to the Nernst-Thomson relation between dissociating power and the dielectric constant of a solvent, Walden finding that if the same electrolyte were dissolved in two different solvents to such concentrations that its degree of dissociation was the same in each, then the volumes of the two solutions, for equal quantity of the solute, were inversely proportional to the cubes (in last year's review this was incorrectly stated as the first powers) of the dielectric constants of the solvents. He further established the fact that at complete dissociation and high dilution the molecular conductivity of the same electrolyte in different solutions is very nearly inversely proportional to the coefficient of viscosity of the pure solvent. Thirdly the heat of dissociation for a given electrolyte was found to be independent of the solvent. Many more interesting details are brought out in the papers, but the above are perhaps the most

:triking features on account of their simplicity and
work is being continued and it will certainly take its pl
:lassics in this branch of inquiry. Bauer (E. Bauer,
:2, 725–6 (1906)) points out that Walden's results supp
which both he and Malmström (R. Malmström, *Z. Elek*
)09 (1905); E. Bauer, *Z. Elektrochem.*, **11**, 936–38 (
riously made upon theoretical grounds, that the ioni
of a binary electrolyte in two immiscible solvents after
partition equilibrium between the two solutions shoul
of the cube of the dielectric constants of the solvents.
ng also requires that the solution pressure of a metal in
be proportional to the cube of the dielectric constant
and consequently, the order of elements in the absolut
should be independent of the solvent. Van Laar (J.
physik. Chem., **58**, 567–74 (1907); **59**, 212–17 (1907)) sho
results corroborate and explain the relation between solu
:iation empirically established by Abegg and Bodlan
the equation of Luther connecting distribution and disso
The high migration velocity of ions common to solute
:xplained by Danneel (see THIS JOURNAL, **28**, 904)
studied by Hantzsch and Caldwell (A. Hantzsch and Ker
Z. physik. Chem., **58**, 575–84 (1907)) using formic and
pyridine as solvents. In conformity with the theory adva
they find pyridinium salts in pyridine, formates in formic
n acetic acid all show abnormally high migration velo

Another long and praiseworthy campaign which is
orth positive results of great importance is the direct
osmotic pressure undertaken by Morse and Frazer with
students (H. N. Morse, J. C. W. Frazer and students, *A*
)0–6; **28**, 1–23; **29**, 173–4; **32**, 93–119; **34**, 1–99; **36**,
)24–60, 425–67, 558–95; **38**, 175–226). After sev
devoted to perfecting the Pfeffer cell and auxiliary app
nique has been reduced to a certainty and a wonderf
accuracy secured. In the past, the lack of this very tec
is, perhaps too willingly, to rely entirely upon the in
measurement by freezing- and boiling-point displacement
and electrochemical measurements, and we have come
fact that these, though perhaps more convenient, are
measures of the quantities sought. For instance in a
1 mg. molecule of solute per liter produces only 0.00
the freezing-point but would still represent on an oil co
an osmotic pressure of 10 cm. We must look to direct
measurements to determine the very high molecular we
This must eventually form another important link in the
typical solutions and suspensions referred to in an earli
article. In this same connection, reference should here
work of Berkeley and Hartley (Earl of Berkeley and
Proc. Roy. Soc., London, A, **78**, 68; also *Phil. Trans.*, **206A**,
who have succeeded in carrying the measurements for ca
up to pressures of 135 atmospheres. Morse and Fra
published results obtained by their methods on a wid

solutions and still more data of a similar character are promised in the near future. One of the most interesting results of the measurements thus far published, at least from a theoretical standpoint, is the fact that it is apparently the volume of the pure solvent rather than that of the finished solution which must be multiplied by the osmotic pressure to give a constant; or as they express it, we should use the "weight normal" rather than the "volume normal." The molecular osmotic pressures which they have measured at 20° are some 2 to 4 per cent. greater than the corresponding molecular gas pressures, while at 0° they are from 6 to 11 per cent. higher. The authors carefully refrain, however, from drawing general conclusions until they shall have extended their measurements to a wider range of temperatures.

An attempt has been made by van Laar (J. J. van Laar, *Proc. Acad. Wet. Amsterdam*, **21**, 53–63 (1906); *Physik.-chem. Centr.*, **4**, 11) to establish the same "weight normal" relation from a thermodynamic standpoint, the theoretical values thus obtained agreeing well with Morse and Frazer's measurements. Another relation pointed out by van Laar is that we are led to expect that the divergence from the $PV = RT$ law will be in opposite senses in the gas and osmotic pressures for most systems. Caldwell (R. J. Caldwell, *Proc. Roy. Soc.*, *A* **78**, 272–95 (1906)) in studying the effect of salts and non-electrolytes upon the inversion of cane sugar by acids also points out how much simpler relations are obtained by referring concentrations to equal quantities of solvent. This paper, together with one by Armstrong (H. E. Armstrong, *Proc. Roy. Soc.*, *A* **78**, 264–71 (1906)) dealing further with the same data, aims to establish the association of solvent and solute in contra-distinction to dissociation of the solute as a general explanation for the peculiarities of electrolytes. Both papers contain much very suggestive matter, however little one may agree with their main contention. The electrolytic dissociation theory in fact has been steadily absorbing of late many of the original concepts of its old opponent, the so-called hydrate theory. A good illustration of this is to be found in H. C. Jones's work on hydrates in solution which has recently been collected and published in book form by the Carnegie Institution of Washington. Another paper touching the same subject by Bousfield (W. R. Bousfield, *Proc. Roy. Soc.*, *A* **77**, 377 (1906) also *Phil. Trans.*, **206***A*, 101–59) presents experimental data in support of his formula (W. R. Bousfield, *Z. physik. Chem.*, **53**, 257–313 (1905)) for the diameter of the hydrated ion at different dilutions of the solution and shows how this may be directly connected with such properties as migration velocity, viscosity, degree of dissociation, density and refractive index.

The subject of photochemistry has come to stand further and further apart from the other divisions of physical chemistry chiefly because, in the latter, it has been the study of reversible processes which have served to bring out the logical connection between apparently unrelated phenomena, while in photochemistry until very recently such processes were almost unknown. In other words in the great majority of laboratory reactions brought about by the action of light, its function may be compared to that of a catalyzer, in that it removes passive resistances from reactions already potentially possible rather than making permanent contribution itself to the free energy of the system. When we stop to

ze that the photochemistry of chlorophyll ac
nic world absolutely depends, represents on th
rent type of process, in which radiant energy is
chemical energy and stored as such, the un
he subject are apparent. The first noteworthy
by Luther, Wiegert and Wilderman was cited
IS JOURNAL, **28**, 909 (1906)). Since then a gr
ect has manifested itself. Luther and Wiegert
k on anthracene and dianthracene (R. Luthe
ik. Chem., **53**, 384–427 (1905)) and Wilderman (
. *Soc. London*, **206A**, 335–401; also *Z. physik*
-5 (1907)) has also published a second very exte
ts on the action of light on a series of galvanic cell
, *Ann. Physik*, **13**, 464–76 (1904)) pointed ou
formation of ozone by various forms of electri
in the main a photochemical process due to
t light thus produced. This has since been
il and quite recently Regener (E. Regener, *An*
1906)) and Russ (F. Russ, *Z. Elektrochem.*, **12**
m that ultraviolet light of wave length 200–30
oxygen, while light of still shorter wave len
rse reaction. The simplicity of the substance h
this unique relation to the different portions
reaction an exceptional importance. In this
d in passing, that Ladenburg and Lehmann (
mann, *Ann. Physik*, **21**, 305–18 (1906)) ha
ain transitory bands in the absorption spect
h they attribute to a still more unstable allo
gen. Among the most suggestive of recent c
retical standpoint are two papers by Trautz
., **4**, 160–72, 351–59 (1906); also *Z. Elektroc*
hich he points out the close relation between re
inescence and those whose velocity is affected l
omplete thermodynamic equilibrium must be ra
"black body." If the system has not reache
, Trautz believes it highly probable that t
tion will not be that of the ideal black bod
the black body spectrum for the temperatu
es sufficiently great for us to detect, we have e
tion or a case of chemical luminescence depe
hich the equilibrium between radiation and al
further pointed out under what restrictions
pplied to photochemical reactions and what ty
be expected, experimental evidence for som
ented. The small temperature coefficient of th
tochemical reaction has often been pointed out, an
e it probable that this quantity is larger the furthe
spectrum the region of photochemical sensitiv
tal confirmation of the view, new data on the
gallol solution are presented. In the dark this
nescence, and it is powerfully accelerated by re
all, by violet. Its temperature coefficient is al

croft (W. D. Bancroft, *J. Physic. Chem.*, **10**, 721–28 (1906)) has lately attacked the general problem of photochemistry from still another aspect, pointing out how by treating each active color of light as a new variable comparable with temperature and pressure, the phase rule may be generalized to include photochemical systems even though these merely represent stationary states and not true thermodynamic equilibria. In illustration and confirmation of this treatment one of his students (G. A. Rankin, *J. Physic. Chem.*, **11**, 1–8 (1907)) has studied the equilibrium of rhombic and amorphous sulphur in carbon bisulphide under the influence of light of varying intensity. Another reversible photochemical reaction has lately been reported by Dewar and Jones (J. Dewar and O. H. Jones, *Proc. Roy. Soc. Lond.*, **79***A*, 66–80 (1907)) in the case of iron tetra- and pentacarbonyls in presence of carbon monoxide. It appears, on the whole, to resemble closely the case of anthracene and dianthracene studied by Luther and Wiegert. In closing, we must not omit mention of the extremely interesting work of Usher and Priestley (F. L. Usher and J. H. Priestley, *Proc. Roy. Soc. Lond.*, **77***B*, 369 (1906), and **78***B*, 369 (1906)) on the primary reactions of the chlorophyll assimilation. They have apparently been able through very ingenious technique to experimentally realize outside of the plant the much looked-for lower aldehyde stage of the process. The importance of this question and the experimental difficulties are both so great that independent confirmation and extension of the experiments are much to be desired. The purely catalytic action of light has also been studied by itself of late by Wiegert (F. Wiegert, *Ann. Physik*, **24**, 55–67 and 243–66 (1907)), both from the theoretical and from the practical side. The reactions between chlorine, carbon monoxide and phosgene fall in this category. On the whole, it seems not too much to hope that we are rapidly approaching an epoch in photochemistry similar to that which electrochemistry passed through some twenty or thirty years ago when it was first really made an integral part of general physical chemistry. May it not be that in the process of this development, photochemistry, like electrochemistry, will furnish us with a new wealth of experimental and theoretical methods for attacking the old problems of general chemistry?

When we come to consider the results of the mere application of physicochemical principles and methods to other branches of chemistry we meet a mass of material which, to do justice to, would carry us far beyond the scope of the present review, but it may still not be out of place to note a few suggestive cases, although such a selection must of necessity be rather an arbitrary one. Toward the problem of protein synthesis Taylor (A. E. Taylor, *J. Biol. Chem.*, **3**, 87–94 (1907)) and Robertson (T. B. Robertson, *Ibid.*, **3**, 95–9 (1907)) have each contributed an example of the reversal of the process of protein digestion, the former working with protamine sulphate and trypsin from the liver of the clam, and the latter with certain stages in the digestion of casein by pepsin. It is instructive to note that both authors were led to their respective methods by purely physicochemical lines of reasoning. The first paper also contains a good set of references to earlier work on reversions of physiological interest. Still another instance of the reduction of a biochemical process to physicochemical control is offered by the work of Buchner, Meisenheimer and Shade (E. Buchner, J. Meisenheimer and H.

Shade, *Ber.*, **39**, 4217–31 (1906); also H. Shade, *Z.* ; 1–46, **60**, 110 (1907)) who have studied the ferment colloidal platinum solutions and shown that the progre is entirely comparable to that of the ordinary yeast fer the dynamical treatment of the process they are furt out the probable type of the intermediate stages of t the work on establishment of a convenient absolute sc alkalinity by the use of indicators standardized by ments, which was begun by Friedenthal (Friedenthal, *Z* 114–9 (1904)) and Salm (E. Salm, *Ibid.*, **10**, 34 99–101 (1906)) has been added a valuable set of d Salm, *Z. physik. Chem.*, **57**, 471–501 (1906)) covering indicators. A much needed thorough systematization of the constitution of alloys which was commenced l Tammann, *Z. anorg. Chem.*, **37**, 303–13. The subs this series have also appeared from time to time in t five years ago, now comprises over fifty papers by hims students, covering a large number of the important bi similar systematic work is just beginning to be und in ternary systems (R. Sohmen and A. v. Vegesack, *Z.* 257–83; **60**, 507–9; also Jänecke, *Ibid.*, **59**, 697–7 (1907)). Of course the systems having iron as one co some time past attracted much attention, but even he workers have, for the most part, centered their activi of special problems. A movement toward a broader whole subject seems, however, to have set in and is bein supported by several of the leading institutions and so Closely related to these metallurgical problems are the ge of rock formation, and here may be noted the work o Laboratory of the Carnegie Institution of Washingto results have already appeared in THIS JOURNAL (A. L Shepherd, THIS JOURNAL, **28**, 1089–1114 (1906)). In this ena of supersaturation, superfusion and vitrification gr the problems. These latter phenomena in themselves receive more direct investigation. Young and Burke (W. E. Burke, THIS JOURNAL, **28**, 315–47; **29**, 3 have reviewed the older work and pointed out som Miers and Isaac (H. A. Miers and Miss F. Isaac, *Proc. A* **79**, 322–50 (1907)) working with mixtures of salol determined the condition for various labile and metast tween a pair of components, both of which show st They also discuss briefly the bearing of the work on geological problems. In this connection for sake of comp may be made of the older work of Guertler on fusion (W. Guertler, *Z. anorg. Chem.*, **40**, 225–53 (1904)), the of devitrification (W. Guertler, *Ibid.*, **40**, 208–79 (1904)) points of the alkaline earth borates (W. Guertler, *Ibid.*, that of Zschimmer's paper on the properties of various gl mer, *Z. Elektrochem.*, **11**, 629–38 (1905)) and Doelter's li genesis" (Die Wissenschaft Sammlung Hft. 13, Braun (1906)).

CORRECTION.

The Relative Solubility of the Silver Halides and Silver Sulphocyanate.—In Table I of this paper (THIS JOURNAL, 30, p. 72) the ratio of the solubility of silver chloride to silver sulphocyanate appears in an inverted form. The mean ratio calculated from the table should read $\frac{S_{AgCNS}}{S_{AgCl}} = 0.0748$.

ARTHUR E. HILL.

NEW BOOKS.

A Text-Book of Electro-Chemistry. By MAX LE BLANC. Translated from the Fourth Enlarged German Edition by WILLIS R. WHITNEY and JOHN W. BROWN. New York: The Macmillan Company. Price, $2.60 net.

Since the first edition of Le Blanc's treatise appeared in 1895 it has been accepted the world over as the standard text-book of electrochemistry. In the succeeding editions the author has aimed to keep pace with the rapidly growing science. It is doubtful whether the resulting growth of the volume to more than double the original size has increased the value of the book as a text-book, but it has provided a remarkably handy and comprehensive compendium of electrochemical knowledge.

The style remains the style of a text-book, and the subject will seem easier to the reader than it is in reality. Weak points in the theory are slurred over. The recent critique of Jahn, the question as to the correctness of the ionization values calculated from the conductivity, the enormous deviation of strong electrolytes from the mass law, receive but scant attention. It has been the misfortune of the ionic theory that its advocates have seldom been satisfied with pointing out its unquestionable triumphs, but have claimed for it a perfection which it has not yet attained.

The author has succeeded to an extraordinary degree in bringing his work up to date. Important investigations which appeared even up to within a few months of the date of publication of the book are mentioned and frequently their results are incorporated in the text.

Occasional misstatements occur, as the one on page 181 that "the 'relations' between the solution pressures of various metals are independent of the nature of the solvent, and, moreover, always possess the same value." As a rule, however, the statements are accurate and reliable. This, unfortunately, is not true of the last chapter, in which the so-called decomposition potentials are discussed. The greater part of this chapter is devoted to an attempted explanation of phenomena which have been shown to be as purely subjective as the N-rays of Blondlot.

The English edition is rather more than a translation. Explanatory and supplementary paragraphs have been added, many new illustra-

tions have been introduced, and the translators have used throughout a new system of notation, devised more methodically than any now in use. They have done an important service in thus calling attention to the need of a rational notation in electrochemistry, whether or not the special system which they propose be ultimately adopted.

GILBERT N. LEWIS.

J. G Gentle's Lehrbuch der Farbenfabrikation, revised and enlarged. By DR. BUNTROCK, Erster Band, Die Erdfarben. Braunschweig: Friedrich Viewig und Sohn 1906. Price, 6 marks.

The preparation of this book was undertaken by Dr. Buntrock at the solicitation of the publishers, Friedr. Viewig und Sohn, and the manuscript of this first part, covering the mineral colors, was delivered to them according to the preface, by the author at the close of 1904, and according to the inscription of the publisher was published September 1, 1906. In view of the very rapid progress being made in the industries, much of the apparatus and some of the methods as well as the use of some of the products described have become obsolete, and the book will therefore be found by no means up to date by those engaged in the industries and hardly a safe guide to those seeking direction in them.

This first volume is divided into five parts treating principally of the mechanical treatment of crude mineral colors to prepare them for use in the arts. Chapter V treats of the chemical changes which the earth colors undergo under various conditions. The other chapters treat respectively of the mechanical means for preparation of these colors, as follows: Elutriation and elutriating apparatus, drying and drying apparatus, milling and mills, bolting and mixing, and the apparatus needed therefor. The apparatus described is such as is usually employed in the industries for the operations mentioned, and it must be said that the forms of construction described and recommended are rather crude as indicated in the illustrations presented. Many of the illustrations of apparatus are to be found in better shape in the catalogues of the manufacturers named in the book, yet for those desiring knowledge regarding the sources from which the apparatus and machines can be obtained the book is by no means a bad guide. Yet this much may be said also of the advertising pages of the current technical chemical journals, while the information offered regarding the mineral colors may be found quite as fully developed and in as reliable a form in most of the encyclopedias and works already at hand in our libraries, public and private.

The part now published closes with extensive advertisements of makers of the machinery described in the text, preceded by an index of these advertisements arranged alphabetically. The book is by no means up to the high standard of the usual publications of Viewig und Sohn.

WM. MCMURTRIE.

Der Nahrungsmittelchemiker als Sachverständiger, Anleitung zur Begutachung der Nahrungsmittel, Genuszmittel und Gebrauchsgegenstände nach den gesetzlichen Bestimmungen mit praktischen Beispielen von PROFESSOR DR. C. A. NEUFELD, Oberinspektor der Kgl. Untersuchungsanstalt für Nahrungs- und Genuszmittel zu München. Berlin: Verlag von Julius Springer. 1907. xix+477 pp. Price, unbound, Mark 10; bound, Mark 11.50.

The primary object of this book is to guide the food chemist in interpreting his analyses and in making suitable recommendations to the court. It is also designed to aid physicians, court officers and other officials who may be called upon to deal with food problems in a legal way. Descriptions of methods are not included.

The book contains a vast store of information touching the source and preparation of foods—their composition, adulteration, imitation and deterioration—and also contains numerous examples illustrating the practical application of this knowledge.

The General Part of the work consists of an introduction with remarks on the purposes of food control, methods of analysis, and standards, chapters on official reports and decisions, and one chapter on the general composition of foods.

The Special Part is divided into twenty-one chapters on the different classes of vegetable and animal foods and a final chapter on toys, cooking utensils, paints, cosmetics and petroleum products.

As a rule each food or class of foods is considered under the following heads: 1. Definition, Origin, Methods of Preparation and Preservation, Composition, and Standards, including the United States Standards. 2. Forms of Adulteration. 3. Imitations. 4. Forms of Damage. 5. Characters Injurious to Health due to Damage, Adulteration, etc. 6. Practical Examples with Analytical Data; Interpretation of Results; Decisions under German Law.

Although the data is in the larger part German, the book will prove a valuable addition to the library of the American food chemist and should also be within the reach of others interested in the manufacture and inspection of foods. A. L. WINTON.

Chapters on Paper Making. By CLAYTON BEADLE. Vol. I., 1904, Vol. II., 1906., H. H. G. Grattan, London; Vol. III., Vol. IV., 1907, Crosby Lockwood & Son, London. Price, $2.00 per vol.

These four small volumes constitute an important contribution to the chemical technology of paper-making. As a necessary consequence of the method by which the subject matter is developed, the treatment is fragmentary and disjointed, but in spite of this regrettable lack of sequence the student of paper-making will find in these "chapters" a great amount of useful information and suggestive discussion which is not to be found elsewhere.

Vol. I comprises ten lectures delivered before the Battersea Polytech-

nic Institute and dealing with various special phases of
of paper-making and the chemical and physical properties

Vol. II opens with a thoughtful discussion of Techn
as Applied to Paper-making, while the body of the volu
of the carefully considered answers made by the author t
propounded by the City and Guilds of London Institute
who had taken its Course in Paper Manufacture. As tc
themselves it may be said that very few American pape
tendents could hope to pass them with credit. Mr. Be
cover in what is usually an eminently practical way ma
which paper-makers generally have only the most empir
and as to which it is only fair to say they have few sour
tion.

Volumes III and IV are the outcome of the publicatio
Pulp of a series of test questions on paper-making techn
to workers in English mills. These questions develope
ingly frank and intelligent discussion of the subjects p
in these last two volumes Mr. Beadle has brought tog
of the best answers to each question and has extended a
whole by critical discussion and comments of his own.

In spite of the serious handicap which the method of
imposed on the author, these volumes will well repay ca
all who have to do with the art of paper-making. A

The Principles of Copper Smelting. By EDWARD DYER PETE
Metallurgy, Harvard University. Hill Publishing Co., New Y
Price, $5.00.

Whoever will carefully read through every page of th
pages will undoubtedly have become acquainted with
upon which the modern practice of copper smelting is bas
hardly, however, agree with the statement that it repre
down of principles; rather would he be likely to conside
planation of these principles could have been made con
concise. This extended style is no doubt admirable in a
but makes continuous reading rather wearisome. It is
a most instructive book. The facts are clearly stated, a
gone into thoroughly, examples and problems being co
to elucidate the various points, and the influence of busi
tions is kept constantly in view. The work is divided int
ters, embracing: Methods and Collectors; First Principle
Principles of Roasting; Chemistry of Smelting; Practice
Blast Furnace Smelting; Reverberatory Smelting; Py
Practical Study of Slags; Matte; Production of Metallic
Matte; Refining of Copper; Principles of Furnace Buil

tions of Thermochemistry; Miscellaneous and Commercial. The chapter on blast furnace smelting contains a very interesting description of the development of the gigantic furnaces constructed by E. P. Matthewson at Washoe, Anaconda, Montana, smelting 3,000 tons of charge per 24 hours. The chapters dealing with pyrite smelting are largely written and are reviewed by R. Sticht, of the Mt. Lyell mine in Tasmania. Throughout the parts dealing with Bessemerizing methods, it is disappointing to find that no credit is given to the pioneer work of the recently deceased John Holloway, of London (in whose laboratory the reviewer found his first occupation), who clearly foresaw, and endeavored to put in practice the principles of these methods, and from the adoption of which others have received the rewards. The chapter on Thermochemistry is written by Prof. Joseph W. Richards, of Lehigh University. In the portion dealing with the refining of copper, but passing mention is made of the electrolytic methods, as they are of very special nature, and the art has a literature, though a meagre one, of its own. While the book is primarily intended for students, and for those who have not an exact knowledge of chemistry, it should be found useful to all who have interests in the mining, refining, or chemistry of copper.

T. LYNTON BRIGGS.

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DUCHEMIN, R. LA DÉNATURATION DE L'ALCOOL en France et dans les principaux pays d'Europe. Paris: 1907. 8vo. 280 p. M. 6,80.

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FIFTEENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED DURING 1907.

BY F. W. CLARKE.

Received January 24, 1908.

Although the number of new atomic weight determinations published during the year 1907 has not been large, the quality of the work done was remarkably high. Some of the determinations are of fundamental importance, as, for example, those of hydrogen, nitrogen, sulphur, potassium and lead. Sulphur and lead are especially noteworthy, on account of their divergence from the older measurements. The data now available are as follows:

Hydrogen.

Noyes[1] has made complete syntheses of water in five series of determinations. The first series was defective, and is therefore not published by the author. For the other series very complete details are given, which would take too much space for repetition here. Noyes's corrected and final data are as follows:

SECOND SERIES, HYDROGEN FROM SULPHURIC ACID, WEIGHED TWICE.

			At. wt. H.	
Weight H.	Weight O.	Weight H_2O.	H : O.	H : H_2O.
3.72565	29.57891	33.30408	1.00765	1.00767
3.80318	30.18400	33.98748	1.00800	1.00799
3.75873	29.83358	33.59127	1.00792	1.00795
2.96328	23.51987	26.48379	1.00792	1.00790
2.11395	.....	18.89214	.....	1.00795
3.53136	28.02910	31.56024	1.00791	1.00792
3.53959	28.09619	31.63554	1.00785	1.00786
		Mean,	1.00787	1.00789

[1] This Journal, 29, 1718.

THIRD SERIES, HYDROGEN FROM SULPHURIC ACID, OXIDIZED BY COPPER OXIDE.

Weight H.	Weight O.	Weight H_2O.	At. wt. H. H : O.	At. wt. H. H : H_2O.
2.44279	19.39757	21.84042	1.00746	1.00746
2.18739	17.36305	19.55117	1.00784	1.00780
2.75129	21.84345	24.59389	1.00764	1.00768
4.00062	.....	35.75073	.....	1.00803
4.04057	32.07689	36.11762	1.00772	1 00772
		Mean,	1.00767	1.00774

FOURTH SERIES, HYDROGEN AND OXYGEN FROM SULPHURIC ACID COMBINED BY PALLADIUM.

Weight H.	Weight O.	Weight H_2O.	At. wt. H. H : O.	At. wt. H. H : H_2O.
2.27916	18.08455	20.36128	1.00823	1.00830
4.12734	32.76527	36.89043	1.00774	1.00780
4.17556	33.13449	37.30787	1.00818	1.00821
4.19346	33.27384	37.46453	1.00822	1 00831
2.30746	18.30863	20.61357	1.00825	1.00839
4 59692	36.48543	41.08162	1.00795	1.00797
4.63625	36.79354	41.42905	1 00806	1.00808
4.57274	36 28696	40 85834	1.00813	1.00817
		Mean,	1.00809	1.00815

FIFTH SERIES, HYDROGEN AND OXYGEN FROM BARIUM HYDROXIDE, COMBINED BY PALLADIUM.

Weight H.	Weight O.	Weight H_2O.	At. wt. H. H : O.	At. wt. H. H : H_2O.
4.61180	36.60909	41.22105	1.00779	1.00779
4.62358	36.69575	41.31647	1.00798	1.00806
4 59853	36 50484	41.10212	1.00776	1.00780
4.55832	36.17887	40.73904	1.00795	1.00790
4.20399	33.37000	37.57336	1.00782	1.00786
		Mean,	1.00786	1 00788

The mean of all four series, assigned equal weight, is H = 1.00789.

The mean of the 48 determinations, as a single series, is H = 1.00793

The series, however, are not of equal weight, the second and fourth being better than the others. According to Noyes, the value H = 1.00787 is the most probable value to be derived from his determinations Morley's classical syntheses of water, recalculated, give H = 1.00762 Combining this with Noyes's results, the average is 1.00775, which is perhaps better than the determinations of either chemist taken alone.

Silver-Nitrogen.

Richards and Forbes,[1] in a most careful investigation, have effected the synthesis of silver nitrate from pure silver, and so measured the

[1] This Journal, 29, 808.

ratios between Ag and $AgNO_3$. The vacuum weights are given below, together with the ratio Ag: $AgNO_3$: : 100: x:

Weight Ag.	Weight $AgNO_3$.	Ratio.
6.14837	9.68249	157.481
4.60825	7.25706	157.480
4.97925	7.84131	157.480
9.07101	14.28503	157.480
9.13702	14.38903	157.481
9.01782	14.20123	157.480
	Mean,	157.480

A small correction for a trace of water retained by the nitrate reduces this figure to 157.479, which is identical with that obtained by combining all the older data. If now, Ag = 107.930, N = 14.037; but if the recent value for N, 14.008, is correct, then Ag becomes 107.880.

Potassium.

Richards and Mueller[1] have redetermined the atomic weight of potassium by analyses of the bromide. First, the ratio between silver bromide and the potassium salt was measured, with the subjoined results:

Weight KBr.	Weight AgBr.	At. wt. K.
2.19027	3.45617	39.114
4.19705	6.62285	39.113
2.06723	3.26206	39.112
2.58494	4.07889	39.115
	Mean,	39.1135

Second, the ratio between potassium bromide and metallic silver was determined by the usual titration method, as follows:

Weight KBr.	Weight Ag.	At. wt. K.
4.33730	3.93164	39.113
4.18763	3.79587	39.115
4.15849	3.76943	39.116
3.67867	3.33450	39.116
3.60484	3.26776	39.110
4.78120	4.33387	39.118
5.67997	5.14860	39.116
6.41587	5.81571	39.115
2.88134	2.61184	37.113
3.64383	3.30309	39.111
3.12757	2.83504	39.113
	Mean,	39.1143

The value for K was computed with Ag = 107.93 and Br = 79.953. All weights were reduced to a vacuum standard. The final value, ob-

[1] This Journal, 29, 639. The paper is preceded by that of Richards and Staehler on potassium chloride, which was noticed in the report of this committee for 1906. It originally appeared in the *Berichte*.

tained by combining these results with those of Richards and Staehler, is K = 39.1139. Clarke, in his "Recalculation of the Atomic Weights," 1897, from a combination of all the older data, found K = 39.112. The two values are nearly identical.

Sulphur.

The atomic weight of sulphur has been redetermined by Richards and Jones,[1] who employed an entirely new method. Silver sulphate was transformed into silver chloride by heating in gaseous hydrochloric acid. The weights, reduced to a vacuum, are subjoined. In the third column the chloride formed from 100 parts of sulphate is given:

Weight Ag_2SO_4.	Weight AgCl.	Ratio.
5.21962	4.79859	91.934
5.27924	4.85330	91.932
5.08853	4.67810	91.934
5.36381	4.93118	91.934
5.16313	4.74668	91.934
5.08383	4.67374	91.933
5 13372	4.71946	91.931
5.16148	4.74490	91.929
5.19919	4.77992	91.936
5.37436	4.94088	91.934
	Mean,	91.933

From this ratio, if Ag = 107.930 and Cl = 35.473, S = 32.113.
If Ag = 107.88 and Cl = 35.457, then S = 32.069.

Incidentally, the authors discuss the older values for sulphur, and especially those derived from gaseous densities. The latter they regard as subject to serious errors.

Lead.

In a preliminary paper, Baxter and Wilson[2] give the results of their analyses of lead chloride. The data, with vacuum weights, are as follows:

Weight $PbCl_2$.	Weight Ag.	Weight AgCl.	Atomic weight. Ag. ratio.	Atomic weight. AgCl ratio.
4.67691	3 62987	4.82273	207 179	207.188
3.67705	2.85375	.....	207.189	.....
4.14110	3.21408	4.27016	207.173	207.192
4.56988	3.54672	.... .	207.185	.....
5.12287	3.97568	5 28272	207.201	207.181
3 85844	2.99456	3.97949	207.186	207.136
4.67244	3.62628	.....	207.189	....
3.10317	2.40837	3.19909	207.188	207.261
4.29613	3.33407	4.42982	207.202	207.204
		Mean,	207.188	207.193

[1] This Journal, 29, 826.
[2] Proc. Amer. Acad., 43, 365.

The mean of both series is Pb = 207.190,[1] when Ag = 107.93 and Cl = 35.473. This value is much higher than the usually accepted 206.9.

Palladium.

The determinations of Woernle[2] were based upon analyses of palladosamine chloride, $Pd(NH_3Cl)_2$. Two reductions in hydrogen gave the following results:

Weight chloride.	Weight Pd.	At. wt. Pd.
2.94682	1.48493	106.68
1.83140	0.92296	106.70

Five electrolytic determinations yielded the subjoined figures:

Weight chloride.	Weight Pd.	At. wt. Pd.
1.02683	0.51749	106.71
1.22435	0.61708	106.72
1.46735	0.73944	106.69
0.59796	0.30139	106.73
2.64584	1.33329	106.69
	Mean,	106.708

All weights were reduced into vacuum. The antecedent values for H, N, and Cl are not stated.

Nickel and Cobalt.

Barkla and Sadler,[3] studying the absorbability of secondary Röntgen radiations from various metals, which is an atomic function, find regularities to which nickel is an exception. If, however, nickel be given a higher atomic weight than that now assigned to it, the anomalies disappear. Ten measurements of absorbability, compared with the absorbability of rays from other metals, gave, by interpolation, values for Ni between 61.15 and 61.6. These figures can hardly be assigned much weight in comparison with the excellent and more direct chemical determinations.

Parker and Sexton,[4] in a brief note, announce that 15 electrolytic comparisons of cobalt with silver give, in mean, Co = 57.7. The details of this investigation are yet to appear.

Indium.

Mathers,[5] in determining the atomic weight of indium, employed two methods. First, the ratio between $InCl_3$ and 3AgCl was measured gravimetrically, with the following results:

[1] With Ag = 107.88 this becomes 207.090. See this Journal, 30, 194.—EDITOR.

[2] Sitzungsb. phys. med. Soz. Erlangen, 38, 296.

[3] Phil. Mag. [6], 14, 408. Preliminary notice in *Nature*, Feb. 14, 1907. In *Nature* for April 4, Hackett questions the conclusions stated by Barkla.

[4] Nature, Aug. 1, 1907.

[5] This Journal, 29, 485.

Weight $InCl_3$.	Weight AgCl.	At. wt. In.
2.1156	4.11421	114.80
4.95920	9.64176	114.85
1.98175	3.85125	114.95
5.54540	10.77904	114.90
1.46361	2.84557	114.86
4.08602	7.94054	114.96
	Mean,	114.88

Secondly, similar analyses were made of indium tribromide, as follows:

Weight $InBr_3$.	Weight AgBr.	At. wt. In.
2.73494	4.34550	114.89
7.69880	12.23341	114.86
6.27450	9.96917	114.89
5.36642	8.52741	114.85
5.16112	8.20128	114.85
4.98336	7.92009	114.81
	Mean,	114.86

The calculations were made with Ag = 107.93, Cl = 35.473, and Br = 9.953. The author favors In = 114.9 as the value to be accepted.

Tellurium.

The research upon tellurium, by Baker and Bennett,[1] was primarily o determine the homogeneity of the element. Various fractionating rocesses were employed, but tellurium of the same atomic weight was roduced in every case. Two methods, both new, were adopted for the tomic weight determinations. First, TeO_2 was heated with sulphur in ubes of glass, the two ends of the tube being packed with pure silver leaf. Sulphur dioxide was expelled, and from its amount, as measured by the oss of weight, the percentage of oxygen in the TeO_2 was computed. For this purpose the value S = 32.06 was assumed. The determinations y this method fall into three principal series, as follows, representing lifferences in the source of the initial substance: 1. Fractional crystalization of telluric acid from barium tellurate. 2. Fractional crystallizaion of telluric acid from oxidation of the element. 3. Tellurium dioxide repared from tellurium hydride. Vacuum weights are given throughut. The data are as follows:

Series 1.

Fraction.	Weight TeO_2.	Loss SO_2.	Per cent. O in TeO_2.
1	1.51509	0.60838	20.055
2	1.09875	0.44074	20.034
3	1.02150	0.40993	20.046
4	0.90835	0.36472	20.053
5	1.00702	0.40451	20.062
6	1.01515	0.40733	20.044

[1] J. Chem. Soc., 91, 1849.

SERIES 2.

Fraction.	Weight TeO_2.	Loss SO_2.	Per cent. O in TeO_2.
1	1.56837	0.62938	20.046
2	1.07852	0.43257	20.035
3	1.72627	0.69296	20.052
4	2.09253	0.83927	20.032
5	0.83335	0.33465	20.059
6	1.15372	0.46284	20.041
7	1.68618	0.67661	20.045
8	0.90835	0.36472	20.053

SERIES 3.

No.			
1	1.02217	0.41050	20.064
2	0.80697	0.32322	20.051
3	1.32003	0.52992	20.053
4	1.05207	0.42221	20.047
5	1.37043	0.54969	20.032
6	0.95944	0.38511	20.048

Several other experiments, concordant with these, are cited, but without the detailed weighings.

The other method employed consisted in converting tellurium into the tetrabromide by direct union with bromine in an atmosphere of nitrogen. Here again, several series of determinations are given. For brevity, the data are combined in one table:

Series.	Weight Te.	Weight $TeBr_4$.	Per cent. Te.
1	0.61273	2.14933	28.508
	0.56866	1.99354	28.525
	0.59884	2.09951	28.523
	0.57894	2.03040	28.514
	0.54743	1.91899	28.527
	0.33859	1.18732	28.517
	0.56866	1.99354	28.526
	0.47643	1.67025	28.525
	0.56622	1.98597	28.511
2	0.44271	1.55205	28.524
	0.41671	1.46177	28.508
	0.50611	1.77489	28.515
3	0.37382	1.31081	28.519
	0.31895	1.11868	28.512
	0.48931	1.71554	28.522
	0.47156	1.65404	28.510
4	0.40748	1.42867	28.523
	0.62013	2.17449	28.518
5	0.37382	1.31081	28.519
	0.50822	1.78207	28.518
	0.12928	0.45354	28.505
	0.42926	1.50540	28.515
6	0.80348	2.81715	28.511
	0.95309	3.34193	28.512

From the dioxide determinations the authors compute that Te = 127.609. From the bromide syntheses, if Br = 79.96, Te = 127.601. They also give, but without details, several determinations based upon analyses of tellurium tetrachloride. Four fractions of the chloride gave for Te the values 127.58, 127.60, 127.64, 127.62. The commonly accepted value, 127.6, thus receives strong confirmation.

On the other hand, quite different results have been announced by Marckwald.[1] He prepared pure telluric acid, H_6TeO_6, which, by heating under proper precautions, was reduced to TeO_2. His figures, on the basis of O = 16 and H = 1.008, are subjoined.

Weight acid.	Weight TeO_2.	At. wt. Te.
8.6277	5.9884	126.93
12.2680	8.5135	126.84
13.0051	9 0244	126.80
8.6415	5.9947	126.65
8.4588	5.8696	126.80
8.0113	5.5599	126.94
	Mean, excluding No. 4.	126.86

From the sums of the weights Marckwald, rejecting the fourth determination, computes Te = 126.85. This falls below the atomic weight of iodine, and is in harmony with the periodic law. Since, however, it diverges so widely from many, concordant, higher determinations, it evidently needs corroboration by other experimenters and other methods.

Ytterbium and Lutecium.

According to Urbain,[2] ytterbium is a mixture of two elements, neo-ytterbium and lutecium. The atomic weight of neo-ytterbium is not far from 170; that of lutecium is perhaps a little above 174. Detailed determinations are yet to be made. In a footnote Urbain remarks that the atomic weight of thulium, which is given as 171 in the tables, is certainly below 168.5.

Radium.

Madame Curie[3] has redetermined the atomic weight of radium, with purer material than that used in her former researches, and in larger quantities. The well-known chloride method was employed, with the subjoined results:

Weight $RaCl_2$.	Weight AgCl.[4]	At. wt. Ra.
0.4052	0.3906	226.35
0.4020	0.3879	226.04
0.39335	0.3795	226.15
	Mean,	226.18

[1] Ber., 40, 4730.

[2] Compt. rend., 145, 759.

[3] *Ibid.*, 145, 422.

[4] From the weights of AgCl, 0.00006 gram is to be deducted in each case, representing filter ash.

Calculated with Ag = 107.8 and Cl = 35.4. With Ag = 107.93 and Cl = 35.45, Ra becomes 226.45, or 226.5 in round numbers. It is announced that Thorpe is also engaged upon a redetermination of this constant.

Gaseous Densities.

Gray[1] has determined the density of gaseous hydrochloric acid, and assigns to the weight of one liter, under standard conditions and in latitude 45°, the value 1.6397 grams.

Guye[2] has discussed the data relative to nitrogen and some of its gaseous compounds, and assigns to it the atomic weight 14.010. D. Berthelot,[3] from essentially the same data, finds N = 14.005. In an elaborate discussion of the whole subject, Guye[4] has finally adopted the following figures for the weight in grams of one liter of each gas considered:

O_2	1.42900	CO_2	1.9768
H_2	0.08987	N_2O	1.9777
N_2	1.2507	HCl	1.6398
CO	1.1504	NH_3	0.7708
NO	1.3402	SO_2	2.9266

Air.... 1.2928

Miscellaneous Notes.

Watson,[5] in a brief note, has considered the simultaneous calculation of atomic weights from a group of related ratios. Hinrichs[6] has proposed a graphic method for achieving the same purpose. He has also published several papers[7] in which he seeks to establish integral values for the atomic weights of Br, Mn, and Cl.

A number of writers[8] have discussed relations between the atomic weights. On the question of standards, see Erdmann,[9] and especially Swarts.[10] The latter proposes two methods by which the atomic weights may be connected with the gas equation, and with the absolute system of units. General papers on the subject of atomic weights are by Brauner[11]

[1] Proc. Chem. Soc., 23, 119.

[2] Compt. rend., 145, 1164.

[3] *Ibid.*, 145, 65.

[4] Arch. Sci. Phys. Nat. [4], 24, 34; Journ. Chim. Phys., 5, 203; Compt. rend., 144, 976; Chem. News, 96, 175; This Journal, 30, 143. Other papers, mostly controversial, are as follows: Guye, Compt. rend., 144, 1360; Berthelot, *Ibid.*, 144, 76, 269.

[5] Nature, 77, 7.

[6] Compt. rend., 145, 715.

[7] *Ibid.*, 144, 973; 144, 1343; 145, 58. See also Chem. Zentralb., 1907, 1958.

[8] See Wilde, Manchester Lit. Phil. Soc.,51 [1], No. 2. Stromeyer, *Ibid.*, No. 6. Minet, Compt. rend., 144, 428; Collins, Chem. News, 96, 176; Verschoyle, *Ibid.*, 96, 197; Delauny, Compt. rend., 145, 1279.

[9] Chem. Zeitung, 31, 95.

[10] Bull. Acad. Roy. Belg., Classe des Sciences, 1907, No. 3, p. 212.

[11] Chem. Zeitung, 31, 483.

nd Richards.[1] Richards's paper is in the form of a lecture delivered efore the German Chemical Society.

U. S. GEOLOGICAL SURVEY,
WASHINGTON, D. C.

CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 21.]

HE EQUIVALENT CONDUCTANCE OF HYDROGEN-ION DERIVED FROM TRANSFERENCE EXPERIMENTS WITH NITRIC ACID.

BY ARTHUR A. NOYES AND YOGORO KATO.

Received December 31, 1907.

Contents: 1. Outline of the investigation. 2. Preparation and standardization the solutions. 3. Description of the experiments. 4. The experimental data. Summary of the transference numbers. 6. Summary and discussion.

1. Outline of the Investigation.

In an article published four years ago by A. A. Noyes and G. V. Sammet[2] there were described some transference determinations made with /20, 1/60 and 1/80 normal hydrochloric acid at 10°, 20°, and 30°, which, hen combined with the equivalent conductance of chloride-ion (using ie value of Kohlrausch) yielded for hydrogen-ion a much higher equivant conductance than that which had been derived from the conductivity f acids at high dilutions. Thus the value for hydrogen-ion at 18° deved from the transference experiments was 330, while that of Kohlausch derived from conductivity was 318. This serious divergence ppeared greater than the possible errors in the transference determinaons;[3] and it seemed as if it must be due either (1) to an error in the exapolated values of the equivalent conductance of acids at zero concenation, (2) to the formation of complex ions or some other abnormality f the hydrochloric acid, or (3) to a marked difference in the relative elocities of the hydrogen-ion and the anion, at moderate and at very w concentrations. To test the first of these possibilities, a study of ie effect of the impurities in the water upon the conductance of very ilute hydrochloric and nitric acids was made in this laboratory by H. I. Goodwin and R. Haskell,[4] the results of which showed that, after liminating the effect of impurities as far as possible, a value for the equivant conductance of hydrogen-ion at extreme dilution (315 at 18°) even wer than that previously derived by Kohlrausch (318) was obtained

[1] Ber., 40, 2767.

[2] This Journal, 24, 944–968; 25, 165–168 (1902–3); Z. physik. Chem., 43, 49–7 903).

[3] The experimental results of Noyes and Sammet have recently been fully conmed by those of Jahn, Joachim and Wolff (Z. physik. Chem., 58, 641 (1907)).

[4] Phys. Rev., 19, 369–396 (1904); Proc. Am. Acad., 40, 399–415 (1904). Reewed in Z. physik. Chem., 52, 630 (1905).

In view of these results it did not seem possible that the divergence could be due to the first-mentioned cause. The present investigation was therefore undertaken, in order to test the second explanation, or that being excluded, to estabish the correctness of the third one. It was carried on with the help of a grant from the Carnegie Institution of Washington, and a description of it substantially identical with that here presented forms a part of Publication No. 63 of that Institution.

It was thought that independent transference experiments with another acid, if they yielded results concordant with those with hydrochloric acid, would serve both to exclude any specific error that might arise from complex ion formation or other individual peculiarity of that acid and to confirm the experimental accuracy of the transference data, and that they would thus establish the fact that a marked change in the relative migration velocity of the ions of acids takes place on passing to very low concentrations. Nitric acid was selected as the second acid, since it is of quite a different chemical character.[1] Another purpose of this investigation, bearing directly on the third suggestion mentioned above, was to extend the transference measurements with both acids to a dilution of about 0.002 normal.

2. Preparation and Standardization of the Solutions.

The chemically pure nitric acid of trade was freed from lower oxides of nitrogen by diluting it with two-thirds its volume of conductivity water and drawing a current of purified air through it. It was carefully tested (using 5–10 cc.) for chloride with silver nitrate, for sulphate by evaporation with barium chloride, for ammonia with Nessler reagent, and for nitrite by diluting and adding starch and potassium iodide. These impurities could not be detected at all, or were present only in entirely insignificant quantity. Dilute solutions (from 0.06 to 0.0006 normal) were made up with water having in all cases a specific conductance lying between 0.9 and 1.2×10^{-6} reciprocal ohms at 18°, and were titrated with the help of phenolphthalein against a 0.1 normal solution of carefully purified barium hydroxide. The strength of the barium hydroxide solution was determined gravimetrically both by precipitating with sulphuric acid after neutralizing with hydrochloric acid and by evaporating to dryness with pure nitric acid and weighing the residue of anhydrous barium nitrate after heating to 160°–180°. The two methods gave for the content of the solution in milli-equivalents per kilogram 110.60 and 110.72, respectively; the value adopted was 110.64. Afterwards two other solutions of barium hydroxide were prepared and titrated against nitric acid solutions which had been standardized against the

[1] A single transference experiment has already been made with this acid at 25° at 0.05 normal concentration by Bein (Z. physik. Chem., 27, 44 (1898)).

first barium hydroxide solution. Solution No. 2 contained 119.04, and solution No. 3 contained 58.59 milli-equivalents per kilogram of solution.

The five solutions of nitric acid varying from about 0.06 to 0.006 normal, which were standardized for use in this work against these barium hydroxide solutions, showed as a mean in each case of 5 or 6 closely concordant determinations a content in milli-equivalents per kilogram of solution as follows:

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Content.....	59.22	57.42	18.426	6.809	6.605

The very dilute solutions (approximately 0.002 normal) of nitric and hydrochloric acids employed could hardly be titrated with sufficient accuracy by this method. The concentrations both of the original solutions and of the portions after electrolysis were therefore determined by measuring their conductance by the usual Kohlrausch method in a cylindrical cell with horizontal electrodes, and dividing the corresponding specific conductance by the equivalent conductance of the acid in question at this concentration and temperature. Goodwin and Haskell have recently determined the equivalent conductances at 18° in 0.001 normal solution to be 371.3 for HNO_3, and 375.0 for HCl at 18°, from which follows with the help of Déguisne's temperature-coefficients: 383.4 for HNO_3 and 387.4 for HCl at 20°, which are the values we have used in calculating the original concentrations. The actual conductance measured in the conductivity vessel, the specific conductance, and the concentration in milli-equivalents per liter calculated therefrom were as follows:

	Nitric acid solution.		Hydrochloric acid solution.	
	No. 6.	No. 7.	No. 1.	No. 2.
Actual conductance $\times 10^6$....	2,142	2,094	1,975	2,136
Specific conductance $\times 10^6$...	847.3	828.4	781.3	845.0
Milli-equivalents per liter.....	2.210	2.161	2.017	2.18

The conductance capacity of the conductivity vessel was 0.3956 for all the measurements presented in this article.[3] Hydrochloric acid solution No. 1 was made by diluting quantitatively by weight (with water of conductivity 0.9×10^{-6}) a 0.13737 normal solution which had been standardized by weighing the silver chloride obtainable from it; the concentration calculated from the dilution was 2.015, in close agreement with that derived from the conductivity (2.017). Solution No. 2 was prepared from the same stock solution, which was itself made by treating pure salt with pure sulphuric acid, redistilling the strong acid obtained

[1] Phys. Rev., 19, 381, 383 (1904). These values like all of ours given below were not corrected for the conductance of the water.

[2] Kohlrausch and Holborn, Leitvermögen der Elektrolyte (1898), p. 199.

[3] A 0.009,954 normal potassium chloride solution measured in it showed as an average of several determinations a conductance of 3111.3×10^{-6} reciprocal ohms.

and diluting it; it was proved to be free from non-volatile matter and from sulphuric acid.

3. Description of the Experiments.

The apparatus, consisting of two connecting U-tubes, was almost identical with that used by Noyes and Sammet, and the procedure followed in the transference experiments was nearly the same. Referring the reader therefore to this article[1] for the main features, we will here describe only the modifications adopted in our work. In order to avoid all danger from leakage, the two U-tubes were joined by drawing over their ends two thicknesses of light black tubing, tightly wiring this on, and entirely covering the joint with melted paraffin. The anode consisted of a circular platinum plate, convex downward, soldered with gold to a platinum wire. The cathode was a straight platinum wire which dipped into the solution always less than 1 cm., so that by having the current dense the reduction of the nitric acid was as far as possible prevented. Since the solution weakened around the cathode and concentrated around the anode, to avoid stirring, the cathode arm was filled with liquid nearly to the top, while the anode arm was filled only a few centimeters above the bend and the electrode was placed just below the surface. To keep the solution at this level the anode arm was fitted with a rubber stopper carrying a delivery tube which dipped into an outside vessel of water whose level could be varied.

Given in outline, the method of carrying out the transference experiments consisted in passing a suitable current for three hours and fifteen minutes (except when otherwise noted in the table) through the standard nitric or hydrochloric acid solutions in the apparatus just described, determining the quantity of electricity by means of two silver coulometers placed in series with it, one on either side, dividing the electrolyzed solution into a cathode, an anode, and three middle portions, and titrating each of these with barium hydroxide (or, in the case of the 0.002 normal solutions, measuring the conductance at 20°) to determine the concentration changes. From the analyses of the cathode and anode portions two separate values of the transference number were obtained, and by the analysis of the middle portions it was made certain that no error arose through convection.

The method of procedure at the end of electrolysis was to transfer by means of a pipette the three middle portions to tared wide-mouth Erlenmeyer flasks with rubber stoppers. Then the two U-tubes were separated from each other, stoppered, well cleaned and dried outside, and weighed. The solutions in them were then, after thorough mixing, poured as completely as practicable into tared flasks, again weighed,

[1] This Journal, 24, 946 (1902).

and finally titrated, allowance being made in the calculation for the small portion that remained in the tubes, which were themselves cleaned, dried, and weighed empty. In the titration of all the portions, the quantity of barium hydroxide solution added was determined by again weighing the flasks containing them after exact neutralization with the base. In those cases where the titration was replaced by a measurement of the conductance, each portion was poured in succession into a cylindrical conductance cell with horizontal platinized electrodes 2.5 cm. apart and measured as accurately as possible, using three resistances in the rheostat.

The principal error to be feared was that which might arise in the analysis of the cathode portion through the reduction of some of the nitric acid by the electrolytic hydrogen. To reduce this to a minimum the cathode was, as already stated, made as small as possible. Since careful analytical tests[1] showed (except in one experiment, No. 2, where the cathode was known to be badly arranged) no nitrite or ammonia in the cathode portion or nitrous vapors in the hydrogen evolved, there is good reason to believe that the error from this source was not serious in most of the other experiments. The effect of this error, it may be noted, would be to cause an apparent *increase* in the transference number of the anion when calculated from the cathode change.

In case of the 0.002 normal hydrochloric acid solution investigated there was the possibility of an opposite error from the liberation of chlorine at the anode, which would have resulted in too small a transference number as calculated from the anode change. With so very dilute a solution and the low current density used, there was probably little danger of this; but to detect any such effect, two different forms of anodes were employed—a short platinum wire in Experiments 1–5 (see Table 1) and a platinum disc in Experiments 6, 7, 9, and 10. As the mean results (167.8 and 168.8) with the two electrodes with such different surface areas agreed almost completely, it seems hardly possible that there was a serious error from this source, especially in the latter experiments.[2]

In order to determine what error, if any, might arise in the very di-

[1] These tests were made by adding to 10 cc. of the cathode portion after its neutralization a few drops of pure sulphuric acid and some starch solution containing potassium iodide; by adding to 10 cc. of the neutralized portion a few drops of Nessler reagent; and by conducting the hydrogen evolved at the cathode through a tube containing filter paper moistened with a solution of starch and potassium iodide. All these tests gave a slight positive indication in the one experiment mentioned above but in no other case, though they were tried in most of them.

[2] The cathodes were also varied in form (since the cathode results were considerably higher than the anode results), though there seemed to be no possibility of an abnormal reaction. A platinum disc was used in Experiments 1–5, a spiral wire in 6–8 and a short straight wire in 9–10. The form of electrode had no influence, however. In Experiment 8 a silver anode was used.

lute solutions from contamination during the experiment, a "blank" experiment was made, in which the solution was treated in absolutely the same way as usual except that no current was passed. The stock solution of hydrochloric acid used (No. 2) had a conductance of 21372 and the portion withdrawn at the end of the experiment had conductances as follows: K,[1] 21336; M_K, 21355; M, 21349; M_A, 21349; A, 21356. There was on an average a decrease of 0.1 per cent. Although this would cause a not considerable divergence of the cathode and anode transference numbers, yet it would not appreciably affect their mean; therefore no correction was made for it (except that the use of 21360 as the initial value eliminated it in great measure in the experiments with this solution).

4. The Experimental Data.

The data of the experiments and the calculated transference values for the 0.06–0.007 normal nitric acid solutions are given in Tables 1–3. The first column contains the number of the experiment; the second, the number of the acid solution used; the third, letters representing the different portions submitted to analysis, K signifying the cathode solution, M_K the adjoining middle portion, M the next portion, M_A the portion adjoining the anode, and A the anode portion itself; the fourth, the weight in grams of the separate portions; the fifth contains the number of grams of barium hydroxide solution used in neutralizing the portions after the electrolysis; the sixth, the initial content, expressed in equivalents and multiplied by 10^6, as calculated from the weight of the portion and the standardization value;[2] the seventh, the final content calculated from the barium hydroxide used; the eighth, the change in content of the separate portions; the ninth, the total change in content, which includes the changes in the portions adjoining the cathode and anode;[3] the tenth, the milligrams of silver precipitated in the coulometers; and the eleventh, the calculated transference numbers for the anion multiplied by 1000.[4]

[1] For the meaning of these letters see the next paragraph.

[2] See Section 3. BaO_2H_2 solution No. 1 was used in Experiments 1 to 6; solution No. 2 in Experiments 7 to 26; and solution No. 3 in Experiments 27 to 32.

[3] Except where the change in the adjoining portion was opposite in sign to that in the electrode portion.

[4] The way in which these were calculated may be illustrated with the help of the data obtained in the first experiment. The cathode portion submitted to analysis weighed 214.08 grams and was found to require 107.72 grams of the BaO_2H_2 solution containing 0.11064 milli-equivalent per gram, so that the final content of the portion was the product of these last two quantities or 11.918 milli-equivalents. To determine the original content the weight of the portion is multiplied by the original concentration of the solution (0.05922 milli-equivalent per gram), which gives 12.678 milli-equivalents. The decrease in content in the cathode portion is, therefore, 0.760 milli-equivalent. Adding to this the decrease in the adjoining middle portion (0.005) and dividing by the number of milli-equivalents of silver (523.0/107.93) precipitated

TABLE 1.—TRANSFERENCE DATA FOR 0.058 OR $^1/_{17}$ NORMAL NITRIC A

Experiment No.	Solution No.	Portion.	Weight of portion.	BaO_2H_2 solution used	Initial content.	Final content.	Change in content.	Total change in content.	
1	2	3	4	5	6	7	8	9	
1	1	K	214.08	107.72	12,678	11,918	— 760	— 765	
		MK	74.55	39.86	4,415	4,410	— 5	...	
		M	212.29	113.50	12,575	12,558	— 17	. .	
		MA	186.16	99.67	11,025	11,028	+ 3	...	
		A	303.87	169.51	17,995	18,755	+ 760	+ 763	
2	1	K	224.01	107.59	13,266	11,904	—1,362	—1,375	
		MK	186.40	99.65	11,039	11,026	— 13	...	
		M	185.02	99.01	10,957	10,955	— 2	. .	
		MA	108.02	57.86	6,397	6,402	+ 5	...	
		A	298.46	171.71	17,675	19,002	+1,327	+1,332	
3	1	K	245.61	116.57	14,545	12,898	—1,647	—1,686	1,
		MK	126.48	67.56	7,490	7,451	— 39	...	
		M	163.15	87.31	9,662	9,660	— 2	...	
		MA	137.35	73.59	8,134	8,142	+ 8	...	
		A	268.43	158.32	15,897	17,517	+1,620	+1,628	1,
4	1	K	304.16	147.75	18,012	16,348	—1,664	—1,664	1,
		MK	109.63	58.62	6,492	6,501	+ 9	...	
		M	182.99	97.86	10,837	10,828	— 9	...	
		MA	155.70	83.48	9,221	9,231	+ 10	...	
		A	273.97	161 19	16,224	17,834	+1,610	+1,620	1,
5	1	K	281.68	137.57	16,681	15,221	—1,460	—1,460	1,
		MK	134.58	72.08	7,970	7,975	+ 5	...	
		M	134.20	71.83	7,947	7,947	± 0	...	
		MA	139.90	75.01	8,285	8,299	+ 14	..	
		A	221.38	131.64	13,110	14,565	+1,455	+1,469	1,
6	1	K	304.32	149.65	18,022	16,558	—1,464	—1,464	1,
		MK	127.83	68 43	7,570	7,572	+ 2	...	
		M	136.01	72.74	8,055	8,048	— 7	...	
		MA	132.70	71.50	7,859	7,911	+ 52	...	
		A	244.75	143.75	14,494	15,906	+1,412	+1,464	1,
7	2	K	267.30	122.93	15,349	13,601	—1,748	—1,755	1,
		MK	128.27	66.50	7,365	7,358	— 7	..	
		M	140 92	73.07	8,091	8,085	— 6	..	
		MA	131.81	68.51	7,568	7,580	+ 12	...	
		A	236.68	138.33	13,590	15,305	+1,715	+1,727	1,
8	2	K	256.11	120.13	14,705	13,292	—1,413	—1,429	
		MK	148.68	77.01	8,537	8,521	— 16	...	
		M	141.13	73.15	8,103	8,094	— 9	.	
		MA	132.89	69.05	7,630	7,640	+ 10	...	
		A	274 66	155 27	15,770	17,180	+1,410	+1,420	

in the coulometer, the transference number is found to be 0.1579. The
tion for the change in weight of the electrode portions by the electroly
ference is applied later.

TABLE I (*Continued*).

Experiment No.	Solution No.	Portion.	Weight of portion.	BaO_2H_2 solution used.	Initial content.	Final content.	Change in content.	Total change in content.	Ag in coulometers.	Transference number × 10³.
1	2	3	4	5	6	7	8	9	10	11
9	2	K	295.01	141.78	16,939	15,687	—1,252	—1,255	861.8	157.2
		MK	105.16	54.54	6,038	6,035	— 3	...	...	...
		M	148.18	76.88	8,008	8,506	— 2	...	...	...
		MA	147.77	76.75	8,485	8,492	+ 7	...	...	...
		A	281.13	157.05	16,144	17,376	+1,232	+1,239	861.4	155.2
10	2	K	258.40	124.30	14,837	13,753	—1,084	—1,085	758.2	154.5
		MK	135.90	70.51	7,803	7,802	— 1	...	...	...
		M	143.28	74.35	8,227	8,227	± 0	...	...	...
		MA	139.93	72.63	8,034	8,036	+ 2	...	...	...
		A	253.26	141.29	14,542	15,633	+1,091	+1,093	757.6	155.7
11	2	K	343.52	167.97	19,725	18,584	—1,141	—1,147	783.3	158.1
		MK	148.88	77.20	8,548	8,542	— 6	...	...	...
		M	162.04	84.05	9,304	9,300	— 4	...	...	...
		MA	139.38	72.33	8,003	8,003	± 0	...	...	...
		A	256.25	143.14	14,713	15,838	+1,125	+1,125	783.0	155.0
12	2	K	275.18	133.84	15,801	14,808	— 993	— 996	687.1	156.5
		MK	154.33	80.06	8,861	8,858	— 3	...	...	...
		M	150.66	78.12	8,650	8,644	— 6	...	...	...
		MA	132.84	68.94	7,627	7,628	+ 1	...	...	...
		A	304.76	167.07	17,499	18,485	+ 986	+ 987	686.8	155.1

TABLE 2.—TRANSFERENCE DATA FOR 0.0184 OR $^1/_{54}$ NORMAL NITRIC ACID AT 20°.

13	3	K	288.64	40.98	5,319	4,879	—440	—443	300.7	159.0
		MK	142.34	22.01	2,623	2,620	— 3	..	..	..
		M	180.71	27.93	3,329	3,325	— 4	..	..	..
		MA	150.21	23.24	2,767	2,767	+ 0	..	..	..
		A	321.64	53.39	5,927	6,370	+443	+443	300.8	159.0
14	3	K	305.45	42.31	5,628	5,037	—591	—591	402.0	158.7
		MK	151.88	23.51	2,799	2,799	— 0	..	..	..
		M	..	...	...	...	..	..	..	..
		MA	129.16	20.01	2,380	2,382	+ 2	..	..	..
		A	308.11	52.70	5,677	6,273	+596	+598	401.8	160.6
15	3	K	334.04	46.44	6,155	5,529	—626	—630	420.8	161.6
		MK	157.46	24.34	2,901	2,897	— 4	..	..	..
		M	164.29	25.42	3,027	3,026	— 1	..	..	..
		MA	133.13	20.62	2,453	2,455	+ 2	..	..	..
		A	363.95	61.59	6,706	7,332	+626	+628	421.0	161.0
16	3	K	353.27	49.64	6,509	5,909	—600	—601	400.5	162.0
		MK	161.93	25.06	2,984	2,983	— 1	..	..	..
		M	175.48	27.13	3,233	3,230	+ 0	..	..	..
		MA	136.96	21.23	2,524	2,527	+ 3	..	..	..
		A	299.07	51.23	5,511	6,099	+588	+591	400.5	159.2
17	3	K	342.27	46.04	6,307	5,481	—826	—833	564.6	159.2
		MK	154.70	23.89	2,851	2,844	— 7	..	..	..

TABLE 2 (*Continued*).

Experiment No.	Solution No.	Portion	Weight of portion.	BaO_2H_2 solution used.	Initial content.	Final content.	Change in content.	Total change in content	Ag in coulometers.
1	2	3	4	5	6	7	8	9	10
		M	171.63	26 57	3,162	3,163	+ 1	..	..
		MA	145.82	22.60	2,687	2,690	+ 3	..	..
		A	347.01	60.64	6,394	7,219	+825	+828	564.
18	3	K	280.38	36.50	5,166	4,345	—821	—822	552.
		MK	145.40	22.50	2,679	2,678	— 1	..	..
		M	159.65	24.70	2,941	2,940	— 1	..	..
		MA	135.00	20.97	2,487	2,496	+ 9	..	..
		A	307.95	54.44	5,674	6,480	+806	+815	553
19	3	K	340.61	45.45	6,276	5,410	—866	—870	588
		MK	127.96	19.77	2,358	2,354	— 4	..	..
		M	159.91	24.74	2,947	2,945	— 2	..	..
		MA	152.38	23.65	2,808	2,815	+ 7	..	..
		A	355.91	62.33	6,558	7,419	+861	+868	588.
20	3	K	287.80	39.08	5,303	4,653	—650	—656	441.
		MK	102.36	15.79	1,886	1,880	— 6	..	..
		M	111.64	17.26	2,057	2,055	— 2	..	..
		MA	131.39	20.30	2,421	2,417	— 4	..	..
		A	423.23	70.95	7,799	8,446	+647	+647	441

TABLE 3.—TRANSFERENCE DATA FOR 0.0067 OR $^1/_{150}$ NORMAL NITRIC A

21	4	K	..	...	...	...	..	..	636
		MK	129.36	7.02	881	836	— 45	..	..
		M	159.75	[illegible].84	1,087	1,052	— 35	..	..
		MA	132.01	7.65	899	911	+ 12	..	..
		A	372.55	29.12	2,537	3,467	+930	+942	636
22	4	K	370.41	14.24	2,522	1,696	—827	—850	578
		MK	135.75	7.57	924	901	— 23	..	..
		M	162.43	9.14	1,106	1,088	— 18	..	..
		MA	124.36	7.20	847	857	+ 10	..	..
		A	379.59	[illegible].75	2,584	3,422	+838	+848	578.
23	4	K	383.23	17.51	2,609	2,085	—524	—531	352
		MK	123.40	7.00	840	833	— 7	..	..
		M	142.82	8.09	972	963	— 9	..	..
		MA	113.52	6.54	771	778	+ 7	..	..
		A	406.87	27.60	2,770	3,285	+515	+522	352.
24	4	K	339.32	15.20	2,311	1,810	—501	—507	337.
		MK	123.67	7.02	842	836	— 6	..	..
		M	162.28	9.26	1,105	1,102	— 3	..	..
		MA	1[illegible].23	6.38	757	759	+ 2	..	..
		A	376.62	25.71	2,564	3,061	+497	+499	337.
25	4	K	352.55	16.62	2,401	1,978	—423	—429	281.
		MK	133.83	7.60	911	905	— 6	..	..
		M	140.73	8.00	958	952	— 6		..
		MA	127.78	7.33	870	873	+ 3	..	..
		A	359.34	24.03	2,447	2,860	+413	+416	282.

TABLE 3 (*Continued*).

Experiment No.	Solution No	Portion.	Weight of portion.	$Ba(OH)_2$ solution used.	Initial content.	Final content.	Change in content.	Total change in content.	Ag in coulometers.	Transference number $\times 10^5$.
1	2	3	4	5	6	7	8	9	10	11
26	5	K	348.65	14.68	2,303	1,747	—556	—559	377.5	159.7
		MK	139.89	7.73	924	921	— 3	..	..	..
		M	139.52	7.67	922	913	— 9	..	..	..
		MA	115.36	6.43	762	766	+ 4	..	..	..
		A	393.06	26.49	2,596	3,153	+557	+561	378.0	160.3
27	5	K	391.96	35.02	2,589	2,051	—538	—546	353.7	166.7
		MK	133.43	14.90	881	873	— 8	..	..	..
		M	167.47	18.77	1,106	1,100	— 6	..	..	.
		MA	132.85	14.99	877	878	+ 1	..	..	..
		A	419.[illegible]	56.11	2,771	3,288	+517	+518	353.5	158.1
28	5	K	369.56	31.75	2,444	1,861	—583	—593	397.3	161.1
		MK	136.30	15.19	900	890	— 10	..	..	..
		M	148.75	16.68	983	978	— 5	..	..	.
		MA	116.62	13.27	770	777	+ 7	..	..	..
		A	394.42	54.39	2,605	3,187	+582	+589	397.5	160.0
29	5	K	407.05	36.61	2,688	2,145	—543	—550	371.2	159.9
		MK	128.28	14.34	847	840	— 7	..	..	..
		M	148.07	16.62	978	974	— 4	..	..	..
		MA	129.11	14.64	853	858	+ 5	..	..	..
		A	416.34	56.22	2,750	3,294	+544	+549	371.2	159.6
30[1]	5	K	407.80	39.75	2,693	2,329	—364	—368	236.2	168.2
		MK	112.65	12.64	744	740	— 4	..	..	..
		M	160.22	18.07	1,058	1,059	+ 1	..	..	..
		MA	119.82	13.49	791	791	+ 0	..	..	..
		A	412.34	52.52	2,724	3,078	+354	+354	236.2	161.8
31[2]	5	K	286.25	36.52	2,551	2,140	—411	—417	275.6	163.3
		MK	143.83	16.11	950	944	— 6	..	..	..
		M	148.08	16.59	978	972	— 6	..	..	..
		MA	107.04	12.07	707	707	+ 0	..	..	..
		A	382.47	49.94	2,526	2,926	+400	+400	275.8	156.6
32[2]	5	K	409.57	34.24	2,705	2,006	—699	—703	472.0	160.7
		MK	119.64	13.41	790	786	— 4	..	..	..
		M	164.62	18.49	1,087	1,083	— 4	..	..	..
		MA	131.90	14.96	871	877	+ 6	..	..	..
		A	410.17	58.11	2,709	3,404	+695	+701	472.1	160.3

Tables 4 and 5 present the results obtained with the more dilute solutions, where the concentration was determined by conductance measurements. The first four columns are the same as in the preceding tables.

[1] In this experiment (No. 30) the period during which the solution was electrolyzed was greater than the usual time ($3\frac{1}{2}$ hours), namely, 6 hours.

[2] In these experiments (Nos. 31 and 32) the solution was electrolyzed $4\frac{1}{2}$ hours and 6 hours, respectively.

TABLE 4.—TRANSFERENCE DATA FOR 0.0022 NORMAL NITRIC ACID AT 20°.

Experiment No.	Solution No.	Portion.	Weight of portion.	Actual conductance × 10^6.	Change in conductance × 10^6.	Change in content.	Total change in content.	Ag in coulometers.	Transference number × 10^3.
1	2	3	4	5	6	7	8	9	10
33[1]	6	K	349.79	1,498	—644	—2,336	—2,345	154.5	163.8
		M_K	97.13	2,133	— 9	— 9	...	...	...
		M	151.75	2,139	— 3	— 5	...	...	...
		M_A	118.86	2,156	+ 14	+ 17	...	...	...
		A	389.53	2,707	+565	+2,282	+2,299	154.5	160.6
34	7	K	349.70	1,813	—281	—1,019	—1,021	66.8	165.1
		M_K	119.33	2,092	— 2	— 2	...	...	...
		M	..	2,086	— 8	...	...	...	...
		M_A	123.57	2,095	+ 1	+ 1	...	...	...
		A	359.49	2,358	+264	+ 984	+ 985	66.7	159.3
35	7	K	359.94	1,562	—532	—1,986	—1,988	131.3	...
		M_K	106.04	2,092	— 2	— 2	...	...	...
		M	134.48	2,089	— 5	— 7	...	...	...
		M_A	113.76	2,104	+ 10	+ 12	...	...	...
		A	393.43	2,571	+477	+1,946	+1,958	131.2	161.0
36	7	K	350.57	1,528	—566	—2,058	—2,073	135.5	165.1
		M_K	104.87	2,080	— 14	— 15	...	...	...
		M	132.59	2,090	— 4	— 5	...	...	...
		M_A	115.59	2,105	+ 11	+ 13	...	...	...
		A	386.20	2,603	+509	+2,039	+2,052	135.5	163.4
37	7	K	..	...	...	...	...	134.6	...
		M_K	125.23	2,086	— 8	— 10	...	...	...
		M	134.42	2,095	+ 1	+ 1	...	...	...
		M_A	139.43	2,104	+ 10	+ 14	...	...	...
		A	376.86	2,606	+512	+2,001	+2,015	134.6	161.6

TABLE 5.—TRANSFERENCE DATA FOR 0.0021 NORMAL HYDROCHLORIC ACID AT 20°.

1	1	K	384.26	1,250	—725	—2,862	—2,883	178.6	174.2
		M_K	125.64	1,959	— 16	— 21	...	...	...
		M	135.42	1,971	— 4	— 5	...	...	...
		M_A	126.10	2,000	+ 25	+ 32	...	...	...
		A	389.93	2,658	+683	+2,736	+2,768	178.9	167.1
2	1	K	313.49	1,360	—615	—1,980	—1,988	123.9	173.3
		M_K	132.60	1,969	— 6	— 8	...	...	...
		M	131.29	1,973	— 2	— 3	...	...	...
		M_A	112.29	1,989	+ 14	+ 16	...	...	...
		A	385.67	2,455	+480	+1,902	+1,918	123.9	167.2
3	1	K	372.66	1,466	—509	—1,949	—1,955	120.2	175.8
		M_K	121.26	1,970	— 5	— 6	...	...	...
		M	135.37	1,970	— 5	— 7	...	...	...
		M_A	130.33	1,985	+ 10	+ 13	...	119.8	...

[1] In this experiment (No. 33) the electrolysis was continued for 4½ hours instead of for 3½ hours as usual.

TABLE 5 (*Continued*).

Experiment No.	Solution No.	Portion.	Weight of portion.	Actual conductance × 10^6.	Change in conductance × 10^6.	Change in content.	Total change in content.	Ag in coulometers.	Transference number × 10^3.
1	2	3	4	5	6	7	8	9	10
4	1	K	385.12	1,295	—680	—2,690	—2,738	171.0	173.0
		Mx	115.65	1,935	— 40	— 48	...	...	...
		M	143.10	1,959	— 16	— 23	...	...	...
		MA	126.67	1,995	+ 20	+ 26	...	...	...
		A	430.37	2,577	+602	+2,661	+2,687	170.9	169.7
5[1]	1	K	388.28	1,497	—478	—1,906	—1,917	115.0	180.1
		Mx	122.78	1,966	— 9	— 11	...	...	...
		M	138.55	1,970	— 5	— 7	...	...	...
		MA	122.73	1,975	+ 0	+ 0	...	...	...
		A	424.00	2,383	+408	+1,777	+1,777	114.8	167.0
6	2	K	420.70	1,546	—590	—2,549	—2,574	161.0	172.5
		Mx	121.58	2,116	— 20	— 25	...	...	...
		M	148.97	2,127	— 9	— 14	...	...	...
		MA	102.76	2,163	+ 27	+ 28	...	...	...
		A	458.17	2,664	+528	+2,485	+2,513	161.1	160.5
7[1]	2	K	443.00	1,761	—375	—1,706	—1,710	105.8	174.4
		Mx	122.55	2,133	— 3	— 4	...	...	...
		M	143.52	2,136	+ 0	± 0	...	...	...
		MA	127.24	2,141	+ 5	+ 7	...	...	...
		A	476.09	2,473	+337	+1,648	+1,655	105.8	168.8
8[1]	2	K	436.04	1,862	—274	—1,227	—1,238	78.0	171.6
		Mx	107.32	2,126	— 10	— 11	...	...	...
		M	142.92	2,129	— 7	— 10	...	...	...
		MA	118.21	2,078	— 58	— 70	...	77.7	...
9	2	K	458.82	1,819	—317	—1,494	—1,495	92.7	174.1
		Mx	107.75	2,135	— 1	— 1	...	...	...
		M	160.12	2,133	— 3	— 5	...	...	...
		MA	104.29	2,142	+ 6	+ 6	...	...	...
		A	478.33	2,430	+294	+1,444	+1,450	92.8	168.8
10	2	K	438.20	1,835	—301	—1,355	—1,361	85.0	173.0
		Mx	114.76	2,131	— 5	— 6	..	...	...
		M	143.57	2,132	— 4	— 6	...	...	...
		MA	104.46	2,136	+ 0	+ 0	...	...	...
		A	471.81	2,411	+275	+1,333	+1,333	84.9	169.3

The fifth contains the actual conductance × 10^6; the sixth, the difference between this value and the initial conductance × 10^6 as given at the end of Section 2;[2] the seventh, the corresponding change in content of the whole portion, expressed in 10^{-7} equivalents, obtained by multiplying this difference by the conductance capacity of the vessel (0.3956), dividing by the equivalent conductance values 382.1 for HNO_3 and 385.8 for

[1] In Experiments 5, 7 and 8 the electrolysis was continued for only 2¾ hours.

[2] These initial values are: 2142 for HNO_3 solution No. 6; 2094 for HNO_3 solution No. 7; 1975 for HCl solution No. 1; and 2136 for HCl solution No. 2.

HCl,[1] and multiplying by the volume of the portion (obtained from its weight by multiplying it by 1.0018); and the eighth, the total change of content or the sum of the changes in the electrode portion and the adoining portion. The ninth column contains the milligrams of silver deposited in the coulometers; and the tenth, the transference number for he anion $\times 10^3$.

5. Summary of the Transference Numbers.

The following table contains a summary of the transference numbers lerived from the preceding experiments together with the means deived therefrom. In finding the separate means of the cathode and anode alues a few abnormally high or low values (designated by an asterisk) ave been omitted.[2] To these means in the case of the two most concenrated solutions a correction has been applied to remove a small error ntroduced by the method used for the calculation of the separate values,[3]

[1] These values are those of dL/dc at 0.002 normal, where L represents the specific onductance and c the equivalent concentration. We derived them through a careful onsideration of all the results obtained by Goodwin and Haskell with both acids at 8° between the concentrations of 0.001 and 0.005 normal. The values were first erived at 18° and were found to be 370.0 for HNO_3 and 373.5 for HCl, and these were hen increased with the help of Déguisne's coefficients so as to make them correspond o 20°. It is scarcely possible that the errors in these values exceed 0.3 per cent.

[2] The high cathode values in Experiments 2, 3 and 4 were probably due to reduction by the electrolytic hydrogen, which was proved to have taken place in Experiment . The cathode value in Experiment 22 was omitted since the middle portion showed large change in content.

[3] Namely, in calculating the original content the total weight of the electrode ortion was simply multiplied by the initial content per gram. That weight had owever, been increased, over what it would have been originally, at the anode by the eight of the transferred nitric acid and had been decreased by the electrolysis out of it f the water corresponding to the hydrogen and oxygen evolved; and at the cathode it ad been decreased by the weight of the transferred nitric acid.

By considering the effect of this on the result, it will readily be seen that when any cid of equivalent weight A, transference number n, and original content c in equivalents er gram of solution is electrolyzed as in this case with the production of hydrogen and xygen, and the calculation is made as above (multiplying the total weight of the ortion by c) then the anode transference-number should be increased by the fractional mount $(An-9)c/n$ and the cathode transference number should be increased by the ractional amount Ac. In this case, with the strongest (0.058) normal solution, the orrections, applied (since $A = 63$, $n = 0.156$, and $c = 0.000058$) are +0.03 per cent n the anode value and +0.36 per cent. on the cathode value. With the 0.018 ormal solutions the corrections are one-third of these percentages.

The corresponding correction was not applied by Noyes and Sammet to their esults with hydrochloric acid. It would have the effect of increasing their final value t 0.05 normal (165.69) by just 0.17 per cent. (to 165.96), while at the lower concentrations the correction would be scarcely appreciable.

A more simple way of calculating transference numbers from the experimental lata is to refer the initial content to the weight of water present instead of to that of he whole solution, and to calculate correspondingly the weight of water in the portion

and the results are designated "corrected means." These cathode and anode means have then been combined in the case of the three stronger nitric acid solutions under the assumption that each has a weight inversely proportional to the square of its average deviation (A. D.). Since the cathode values show in all three cases much greater variations, this procedure gives to the anode values a much greater weight, which would be *a priori* desirable since they are not subject to the possible error arising from the reduction of the nitric acid around the cathode. It is in fact very probable that both the larger variations and the greater magnitude of the cathode values are due to this cause. In spite of this source of error, it is to be noted that the mean cathode value exceeds the mean anode value by only 0.9, 0.6, and 1.1 per cent., respectively, in the case of the three more concentrated solutions. Taking into account the fact that almost all other errors affect the two results in opposite directions, we believe the final A. D. values give a fair measure of the probable precision of the final results, which is from 0.2 to 0.3 per cent. for the 0.06 to 0.007 normal nitric acid solutions.

In the case of the 0.002 normal solutions of both acids the divergence of the cathode and anode mean values is much greater, and it seemed best to assign an equal weight to each without reference to the value of

TABLE 6.—SUMMARY OF THE TRANSFERENCE VALUES.

0.058 normal HNO_3 at 20°.			0.0184 normal HNO_3 at 20°			0.0067 normal HNO_3 at 20°.		
Experiment No.	Cathode.	Anode.	Experiment No.	Cathode.	Anode.	Experiment No.	Cathode.	Anode.
1.....	157.9	*157.4	13.....	159.0	159.0	21.....	...	159.8
2.....	*161.4	156.3	14.....	158.7	160.6	22.....	*158.6	158.2
3.....	*161.1	155.6	15.....	161.6	161.0	23.....	160.3	159.5
4.....	*160.6	156.3	16.....	162.0	159.2	24.....	162.2	159.6
5.....	154.5	155.4	17.....	159.2	158.3	25.....	164.3	159.3
6.....	156.0	156.0	18.....	160.5	159.1	26.....	159.7	160.3
7.....	157.7	155.2	19.....	159.5	159.1	27.....	*166.7	158.1
8.....	156.0	155.0	20.....	160.3	158.1	28.....	161.1	160.0
9.....	157.2	155.2	Mean.....	160.10	159.30	29.....	159.9	159.6
10.....	154.[illegible]	155.7	Corrected			30.....	*168.2	161.8
11.....	158.1	155.0	mean.....	160.29	159.32	31.....	163.3	*156.6
12.....	156.5	155.1				32.....	160.7	160.3
Mean.....	156.49	155.53	a. d.....	1.00	0.71	Mean.....	161.44	159.68
Corrected			A. D.....	0.35	0.25	a. d	1.36	0.69
mean.....	157.05	155.58	Final mean.	159.64		A. D.....	0.48	0.21
a. d.....	1.10	0.41	Final A.D. .	0.34		Final mean..	149.96	
A. D.....	0.36	0.12				Final A. D...	0.44	
Final mean.	155.73							
Final A. D..	0.27							

after the electrolysis by subtracting from its total weight the weight of solute found in it; but even then a correction must be applied to the anode portion for the water electrolyzed out of it. The present basis of all such transference determinations is of course the assumption that the water itself does not migrate.

TABLE 6 (*Continued*).

0.0022 Normal HNO_3 at 20°.

Experiment No.	Cathode.	Anode.
33	163.8	160.6
34	165.1	159.3
35	163.5	161.0
36	165.1	163.3
37	...	161.6
Mean	164.4	161.2
a. d.	0.7	1.0
A. D.	0.4	0.5
Final mean	162.8	
Final A. D.	1.2	

0.0021 Normal HCl at 20°.

Experiment No.	Cathode.	Anode.
1	174.2	*167.1
2	173.3	*167.2
3	175.8	..
4	173.0	*169.7
5	*180.1	*167.0
6	172.5	168.5
7	174.4	168.8
8	171.6	..
9	174.1	168.8
10	173.0	169.3
Mean	173.5	168.8
A. D.	0.3	0.1
Final mean	171.1	
Final A. D.	1.7	

its average deviation; for the divergence probably arises in the main from a slight contamination of these very dilute solutions during the experiment, which would affect the cathode and anode values oppositely and about equally. The final A. D. values, which expressed as percentages are 0.7 per cent. for the nitric acid and 1.0 per cent. for the hydrochloric acid, are again a fair measure of the maximum error of which there is any reasonable probability.

6. Summary and Discussion.

The final results of the transference experiments described in this article, as well as of those carried out by Noyes and Sammet[2] with 0.05-0.006 normal hydrochloric acid at 20°,[3] are brought together in Table 7. In this table are also given the values of the equivalent conductance of hydrogen-ion calculated from each transference number and from the most probable values for nitrate-ion and chloride-ion (64.6 and 68.5, respectively) at 20° and extreme dilution.[4] In the last row of the table are given the corresponding values for zero concentration as derived from Goodwin and Haskell's conductivity experiments.[5]

[1] The mean of all the anode values is 168.3 but it seems best to omit the first four in which experiments an anode of small surface was used, and which are somewhat lower perhaps owing to the evolution of a small quantity of chlorine.

[2] Z. physik. Chem., 43, 63 (1903); This Journal, 24, 958; 25, 167 (1902–3).

[3] Corrected for the inaccuracy in their calculation as described in a preceding footnote.

[4] The value here given for the Cl is that derived by Noyes and Sammet from Kohlrausch's conductivity data and the existing transference data for potassium chloride. That for the NO_3 ion we have obtained by subtracting from that for the Cl the difference for these two ions at 20° given by Kohlrausch (*Sitzungsber. königl. preuss. Akad. der Wissensch.*, 1901, 1031). These values have then simply been multiplied by $(1 - n)/n$.

[5] These investigators found for Λ_0 at 18° 377.0 for HNO_3 and 380.1 for HCl. The corresponding values at 20° calculated with Déguisne's coefficients are 389.2 and 392.5 respectively. Subtracting from these the values for the NO_3 and Cl ions (64.6 and 68.5) one obtains the values for the hydrogen-ion given in the table.

TABLE 7.—FINAL VALUES OF THE TRANSFERENCE NUMBERS AND THE EQUIVALENT CONDUCTANCE OF HYDROGEN-ION.

Equivalent per liter.		Transference number $\times 10^3$.		Equivalent conductance of hydrogen-ion from experiments with	
HNO_3.	HCl.	HNO_3.	HCl.	HNO_3.	HCl.
0.058	0.051	155.7	166.0	350.3	344.2
0.0184	0.017	159.6	167.5	340.2	340.5
0.0067	0.0056	160.0	167.1	339.1	341.4
0.0022	0.0021	162.8	171.1	332.2	331.8
0	0	166.0	174.5	324.6	324.0

It will be seen from Table 7 that, except at the highest concentration (0.055 normal), there is substantial agreement between the values of the equivalent conductance of hydrogen-ion derived from the independent transference experiments with the two different acids, and that the (nearly constant) value for the concentration interval between 0.018 and 0.006 normal is nearly 5 per cent. larger than that derived from conductivity measurements at extreme dilution. The reality of this divergence, first discovered by Noyes and Sammet, confirmed as it is on the conductivity side by the investigation of Goodwin and Haskell and on the transference side by the recent determinations of Jahn, Joachim, and Wolff, and by these new experiments with nitric acid, can, we believe, no longer reasonably be doubted. It must therefore be concluded that *the transference number of the anion of acids, and therefore the ratio of the velocity of the anions to that of the hydrogen-ion, is several per cent. larger at very small concentration* (0.001 normal and less) *than at moderate concentrations* (0.05 to 0.005 normal). Thus a change in the relative velocities takes place even after the concentration of the solute has become so small that as a medium the solution scarcely differs from the pure solvent. The fact that higher transference numbers were obtained with the 0.002 normal solutions than with the more concentrated solutions of both acids confirms the conclusion drawn from the comparison with the conductivity data. The values obtained at 0.002 normal show, moreover, that even at this very low concentration the velocities have not yet become identical with those at zero concentration.

This change of the transference number may, of course, arise either from an acceleration of the anion or from a retardation of the hydrogen-ion at very high dilution, or from both causes combined. The facts that salts do not as a rule show any change in their transference numbers after a moderate dilution is reached and that their ionization values calculated from freezing-point lowering and other molecular properties agree with those corresponding to the conductance ratio (Λ/Λ_0)[1] make it probable, however, that it is the fast-moving hydrogen-ion that is

[1] See A. A. Noyes, Z. physik. Chem., 52, 634.

mainly, if not wholly, affected.[1] It is under this (possibly assumption, namely, that neutral ions have the same velocity at and at very low concentrations, that the values, given in Table equivalent conductance of hydrogen-ion at various concentrat derived.

The fact that the values of the equivalent conductance of ion are nearly constant for the interval of concentration o. seems to indicate that these are the normal ones, and that the at lower concentrations arise from some secondary effect of character, determined perhaps by the smallness of the ion-c tion itself.

The results obtained at the highest concentration (0.05 to 0.0 differ in the case of the two acids, which makes it seem probabl variation in the stronger solution is due to some different cause, one of a specific chemical nature, from that which gives rise to t at high dilutions.

As to the bearing of these results on the calculation of ionizati it may be said that in the case of largely ionized acids at mod centrations it seems in the light of now existing knowledge mo priate to divide the observed equivalent conductance of the ac value obtained by adding to the equivalent conductance of that of the hydrogen-ion obtained by the transference experime described at the concentration in question. On the other har case of any acid solution in which the *ion* concentration is less t normal the older value (324 at 20° or 315 at 18°) for hydroger be preferred.

It is of interest to compare the ionization of hydrochloric puted in the manner just stated with that of neutral salts of ionic type, like potassium and sodium chlorides. At the con 0.05 normal the ionization value derived from Kohlrausch's va of the equivalent conductance of the acid at 18° is found to provided the equivalent conductance of hydrogen-ion is taken derived from the conductivity of the acid at small concentratio becomes 0.900 when the equivalent conductance of hydrogen io 6.2 per cent. larger than this, in accordance with the transferen At this same concentration the ionization values for potassiun and sodium chloride, as derived from their equivalent conc are 0.891 and 0.878. The approximate agreement of these va the new one for hydrochloric acid seems to justify the extension ionized acids of the principle that salts of the same ionic type ha same concentration roughly the same degree of ionization.

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[1] It is therefore probable that the decrease in the conductance of s always observed at very high dilutions is not wholly due to impurities in t

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THE CONDUCTIVITY AND IONIZATION OF SALTS, ACIDS, AND BASES IN AQUEOUS SOLUTIONS AT HIGH TEMPERATURES.

A Report by ARTHUR A. NOYES upon a Series of Investigations by A. A. NOYES, A. C. MELCHER, H. C. COOPER, G. W. EASTMAN and YOGORO KATO.

In a previous paper[1] from this laboratory by A. A. Noyes and W. D. Coolidge an apparatus and method were described for the accurate measurement of the electrical conductivity of aqueous solutions at high temperatures. Measurements with solutions of potassium and sodium chlorides were presented and discussed. Further measurements have since been made with these two salts, and the investigation has been extended to other di-ionic salts (silver nitrate, magnesium sulphate, sodium acetate, ammonium chloride, and ammonium acetate), to two tri-ionic salts (barium nitrate and potassium sulphate), to an acid salt (potassium hydrogen sulphate), to certain acids (hydrochloric, nitric, sulphuric, phosphoric and acetic acids), and to certain bases (sodium, barium, and ammonium hydroxides). With most of these substances the measurements have been made at four or more different concentrations varying between 0.1 and 0.002 normal and at temperatures ranging from 18° to 306°.

For the original data and for a detailed description of the experimental methods and of the calculations, reference should be made to Publication No. 63 of the Carnegie Institution of Washington, of a part of which publication this article is a brief summary.[2] Only the final results will be communicated here.

Tables 1 and 2 contain the values of the equivalent conductance of the various substances expressed in reciprocal ohms. The values of the concentration given in the second column express the milli-equivalents of solute per liter of solution at the temperature to which the conductance value refers. (In the two cases of potassium hydrogen sulphate and phosphoric acid, however, the concentration is expressed in milli-formula-weights of solute ($KHSO_4$ or H_3PO_4) per liter of solution, and the values are correspondingly the molal (or "formal") conductances instead of the equivalent conductances). In obtaining these values excepting, however, the cases of the strong acids, the conductance of the water was subtracted, and those for sodium acetate, ammonium acetate, and ammonium chloride have been corrected for the effect of the hydrolysis of the salts. The atomic weights employed were those given by the International Commission for 1905, referred to oxygen as 16.00. The temperature is the

[1] This Journal, 26, 134–170 (1904).

[2] Copies of that publication may be obtained at a cost of $2.50 each, by application to the authorities of the Carnegie Institution.

Substance.	Concentration.	18°.	25°.	50°.	75°.	100°.	128°.	156°.	218°.	281°.	306°.
Potassium chloride.....	0.0	130.1	(152.1)	(232.5)	(321.5)	414	(519)	625	825	1005	1120
	2.0	126.3	146.4	...	...	393.0	...	588	779	930	1008
	10.0	122.4	141.5	215.2	295.2	377.0	470.0	560	741	874	910
	80.0	113.5	...	...	...	341.5	...	498	638	723	720
	100.0	112.0	129.0	194.5	264.6	336.0	415.0	489.5	...	...	...
Sodium chloride.....	0.0	109.0	...	...	...	362.0	...	555	760	970	1080
	2.0	105.6	...	...	...	349.0	...	534	722	895	955
	10.0	102.0	...	...	...	335.5	...	511	685	820	860
	80.0	93.5	...	...	...	301.0	...	450.5	500	674	680
	100.0	92.0	...	...	...	296.0	...	441.5	...	...	...
Silver nitrate.....	0.0	115.8	...	...	...	367	...	570	780	965	1065
	2.0	112.2	...	...	...	353	...	539	727	877	935
	10.0	108.0	...	...	...	337	...	507	673	790	818
	20.0	105.1	...	...	...	325.5	...	487.5	639	...	...
	40.0	101.3	...	...	...	311.5	...	462.0	599	680	680
	80.0	96.5	...	...	...	294.0	...	432.0	552	614	604
	100.0	94.6	...	...	...	289.0	...	...	...	...	...
Sodium acetate.....	0.0	78.1	...	...	...	285	...	450	660	...	924
	2.0	74.5	...	...	...	267.6	...	421	578	...	801
	10.0	71.2	...	...	...	253.3	...	396	542	...	702
	80.0	63.4	...	...	...	221.0	...	340	452	...	...
Magnesium sulphate.....	0.0	114.1	...	...	...	426	...	690	1080	...	...
	2.0	94.3	...	..	..	302	...	377	260	...	...
	10.0	76.1	...	...	...	233.5	...	241.0	143	...	...
	20.0	67.5	...	...	..	190.0	.	195.0	110.5	...	...
	40.0	59.3	..	..	..	160.0	...	158.0	88.5	...	...

TABLE I.—FINAL VALUES OF THE EQUIVALENT CONDUCTANCE OF NEUTRAL SALTS.—*Continued.*

Substance.	Concentration.	18°.	25°.	50°.	75°.	100°.	128°.	156°.	218°.	261°.	306°.
Magnesium sulphate.....	80.0	52.0	...	...	...	136.0	...	133.0	75.2	...	...
	100.0	49.8	...	...	...	129.5	...	126.0	...	...	...
	200.0	43.1	...	...	...	110.5	...	109.1	...	...	...
Ammonium chloride.....	0.0	131.1	152	...	...	(415)	...	(628)	(841)	...	(1176)
	2.0	126.5	146.5	...	...	399	...	601	801	...	1031
	10.0	122.5	141.7	...	...	382	...	573	758	...	925
	30.0	118.1	...	...	...	...	...	...	...	...	828
Ammonium acetate.....	0.0	(99.8)	...	...	...	(338)	...	(523)	...	...	...
	10.0	91.7	...	...	...	299.8	...	456	...	...	...
	25.0	88.2	...	...	...	286.5	...	426	...	...	...
Barium nitrate.....	0.0	116.9	...	...	...	385	...	600	840	1120	1300
	2.0	109.7	...	...	...	352.0	...	536	715	828	824
	10.0	101.0	...	...	...	322.0	...	481	618	658	615
	40.0	88.7	...	...	...	280.0	...	412	507	503	448
	80.0	81.6	...	...	...	257.5	...	372	449	430	...
	100.0	79.1	...	...	...	249.0	...	...	...	...	...
Potassium sulphate.....	0.0	132.8	...	...	...	455	...	715	1065	1460	1725
	2.0	124.8	...	...	...	401.5	...	605	806	893	867
	10.0	115.7	..	...	...	365.0	...	537	672	687	637
	40.0	104.2	...	...	...	320.0	...	455	545	519	466
	80.0	97.2	...	...	...	294.5	...	415	482	448	395.5
	100.0	95.0	...	...	...	286.0	...	...	...	...	...

TABLE 2.—FINAL VALUES OF THE EQUIVALENT CONDUCTANCE OF ACIDS AND BASES.

Substance.	Concentration.	18°.	25°.	50°.	75°.	100°.	128°.	156°.	218°.	260°.	306°.
Hydrochloric acid	0.0	379.0	...	...	...	850	...	1085	1265	1380	1424
	2.0	373.6	...	...	...	826	...	1048	1217	1332	1337
	10.0	368.1	...	...	...	807	...	1016	1168	1226	1162
	80.0	353.0	...	...	..	762	...	946	1044	1046	862
	100.0	350.6	...	...	...	754	...	929	1006	...	...
Nitric acid	0.0	377.0	421.0	570	706	826	945	1047	(1230)	...	(1380)
	2.0	371.2	413.7	559	690	806	919	1012	1166	...	1156
	10.0	365.0	406.0	548	676	786	893	978	...	...	...
	50.0	353.7	393.3	528	649	750	845	917	..	...	...
	100.0	346.4	385.0	516	632	728	817	880	...	...	454[1]
Sulphuric acid	0.0	383.0	(429)	(591)	(746)	891	(1041)	1176	1505	...	(2030)
	2.0	353.9	390.8	501	561	571	551	536	563	...	637
	10.0	309.0	337.0	406	435	446	460	481	53 3	...	...
	50.0	253.5	273.0	323	356	384	417	448	502	...	...
	100.0	233.3	251.2	300	336	369	404	435	483	...	474[1]
Potassium hydrogen sulphate	2.0	455.3	506.0	661.0	754	784	773	754	...	...	...
	50.0	295.5	318.3	374.4	403	422	446	477	...	..	...
	100.0	263.7	283.1	329.1	354	375	402	435	...	...	...
Phosphoric acid	0.0	338.3	376	510	631	730	839	930	...	...	...
	2.0	283.1	311.9	401	464	498	508	489	..	...	...
	10.0	203.0	222.0	273	300	308	298	274	...	...	...
	50.0	122.7	132.6	157.8	168.6	167.8	158	142	...	...	...
	100.0	96.5	104.0	122.7	129.9	128 4	120.2	107.7	..	..	..

[1] These values are at the concentration, 80.0.

TABLE 2.—FINAL VALUES OF THE EQUIVALENT CONDUCTANCE OF ACIDS AND BASES.—*Continued.*

Substance.	Concentration.	18°.	25°.	50°.	75°.	100°.	128°.	156°.	218°.	260°.	306°.
Acetic acid	0.0	(347.0)	...	...	...	(773)	...	(980)	(1165.0)	..	(1268)
	10.0	14.50	...	...	...	25.10	...	22.15	14.70	..	...
	30.0	8.50	...	...	...	14.70	...	12.95	8.65	..	...
	80.0	5.22	...	...	...	9.05	...	8.00	5.34	..	...
	100.0	4.67	...	...	...	8.10	...	...	4.82	..	1.57
Sodium hydroxide	0.0	216.5	...	...	...	594	...	835	1060	..	...
	2.0	212.1	...	..	...	582	...	814	...	..	...
	20.0	205.8	...	...	...	559	...	771	930	..	...
	50.0	200.6	...	...	...	540	...	738	873	..	...
Barium hydroxide	0.0	222	256	389	(520)	645	(760)	847	...	..	...
	2.0	215	...	359	...	591	...	...	...	..	...
	10.0	207	235	342	449	548	664	722	...	..	...
	50.0	191.1	215.1	308	399	478	549	593	...	..	...
	100.0	180.1	204.2	291	373	443	503	531	...	..	...
Ammonium hydroxide	0.0	(238)	(271)	(404)	(526)	(647)	(764)	(908)	(1141)	..	(1406)
	10.0	9.66	...	...	...	23.25	...	22.31	15.56	..	...
	30.0	5.66	...	...	...	13.58	...	12.99	...	..	...
	100.0	3.10	3.62	5.35	6.70	7.47	...	7.17	4.82	..	1.33

true temperature on the hydrogen-gas scale (as derived at the higher temperatures from the determinations of Jaquerod and Wassmer[1] of the boiling-points of naphthalene and benzophenone). The conductance values (Λ_0) at zero concentration were mostly obtained with the help of an empirical function of the form $1/\Lambda_0 = 1/\Lambda - K(C\Lambda)^{n-1}$, which corresponds to the equation $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$, by plotting the reciprocal of the equivalent conductance ($1/\Lambda$) at the various concentrations (C) against $(C\Lambda)^{n-1}$, varying the value of n till a linear plot was obtained, and then extrapolating for zero concentration. For the slightly ionized substances and for some of the others the Λ_0 values were derived from the others by the principle of the additivity of ion conductances; and in a few cases, the values at certain intermediate temperatures were obtained by graphic interpolation; values derived in either of these ways are indicated by enclosure within parentheses.

These conductivity results have interest from a theoretical standpoint mainly in two respects—first, with reference to the equivalent conductance of the ions or their specific migration-velocities; and second, with reference to the degree of ionization of the various substances.

The directly derived values of Λ_0 for the largely ionized electrolytes are summarized in the following table. The substances are arranged primarily according to the ionic type and secondarily in the order in which the Λ_0 values at 18° increase. In adjoining columns are given also the mean temperature-coefficient $\Delta\Lambda_0/\Delta t$ for the successive temperature-intervals and the ratio $\Lambda_{0(S)}/\Lambda_{0(KCl)}$ of the equivalent conductance of the substance in question to that of potassium chloride at the same temperature.

The results given under $\Lambda_{0(S)}/\Lambda_{0(KCl)}$ in Table 3 show that the values of the equivalent conductance for complete ionization in the case of all the di-ionic substances investigated become more nearly equal as the temperature rises, the approach toward equality being rapid between 18° and 218°, but comparatively slow at the higher temperatures. This shows, of course, that the specific migration-velocities of the ions are themselves more nearly equal, the higher the temperature. Complete equality has not, however, been reached even at 306°, but the divergence exceeds 5 per cent. only in the cases of hydrochloric acid, sodium hydroxide, and sodium acetate, which have ions which at 18° move with exceptionally large or small velocities.

The behavior of the tri-ionic salts, potassium sulphate and barium nitrate, is especially noteworthy. Their equivalent conductance increases steadily with rising temperature and attains values which are much greater than those for any di-ionic uni-univalent salt. Thus, at 306°, the value for potassium sulphate is about 1.5 times as great as that for

[1] J. chim. phys., 2, 72 (1904).

TABLE 3.—EQUIVALENT CONDUCTANCE AT ZERO CONCENTRATION.

Temperature.	Sodium acetate. Λ_0.	$\frac{\Delta\Lambda_0}{\Delta t}$.	$\frac{\Lambda_0(S)}{\Lambda_0(KCl)}$.	Sodium chloride. Λ_0.	$\frac{\Delta\Lambda_0}{\Delta t}$.	$\frac{\Lambda_0(S)}{\Lambda_0(KCl)}$.	Silver nitrate. Λ_0.	$\frac{\Delta\Lambda_0}{\Delta t}$.	$\frac{\Lambda_0(S)}{\Lambda_0(KCl)}$.
18	78.1		0.60	109.0		0.84	115.8		0.89
		2.53			3.09			3.06	
100	285		0.69	362		0.87	367		0.89
		2.95			3.44			3.62	
156	450		0.72	555		0.89	570		0.91
		3.40			3.31			3.39	
218	660		0.80	760		0.92	780		0.95
					3.33			2.94	
281	..	3.00	..	970		0.96	965		0.96
					4.40			4.00	
306	924		0.82	1080		0.96	1065		0.95
	Potassium chloride.			Ammonium chloride.			Sodium hydroxide.		
18	130.1		..	130.7		1.01	216.5		1.67
		3.46			3.47			4.60	
100	414.		..	415		1.00	594		1.43
		3.77			3.80			4.30	
156	625		..	628		1.00	835		1.33
		3.23			3.43			3.63	
218	825		..	841		1.02	1060		1.29
		2.86			...			..	
281	1005		..	..	3.81	..	..		..
		4.60							
306	1120		..	1176		1.05		..	..
	Barium nitrate.			Potassium sulphate.			Barium hydroxide.		
18	116.9		0.90	132.8		1.02	222		1.71
		3.27			3.93			5.16	
100	385		0.93	[illegible]		1.10	645		1.56
		3.84			4.64			3.58	
156	600		0.96	715		1.14	847		1.30
		3.87			5.64			..	
218	840		1.02	1065		1.29	..		
		4.44			6.27				
281	1120		1.11	1460		1.45	..		..
		7.20			10.6			..	
306	1300		1.16	1725		1.54			
	Phosphoric acid.			Nitric acid.			Hydrochloric acid.		
18	338		2.60	377		2.90	379		2.91
		4.78			5.61			5.76	
100	730		1.76	826		1.99	860		2.05
		3.57			3.95			4.20	
156	930		1.49	1047		1.67	1085		1.73
		..			2.95			3.90	
218	..		..	1230		1.49	1265		1.53
		..			...			1.82	
306	..		..	..		..	1424		1.27

potassium chloride. This behavior, which at first sigh mal, is in reality in conformity with the principle that ions subjected to the same electric force approach equ temperature; for, assuming that the resistance of the the same for all ions, the velocity of a bivalent ion, ow electric charge, should become twice as great as that o under the same potential-gradient; and correspondingly conductance of a completely ionized uni-bivalent salt s times that of a completely ionized uni-univalent salt markable is, therefore, not the greater values at high t the approximate equality at room temperature of the eq ances of bivalent and quivalent ions, especially of the which might be expected to have not far from the same siz may be due, as has been suggested by Morgan and Kanol large hydration of the bivalent ions.

With respect to the form of the temperature-conducta be seen from an examination of the values of $\Delta\Lambda_0/\Delta t$ th crease of conductance is in case of all the neutral di-io between 100° and 156° than it is between 18° and 100°, and 218°,[3] and, therefore, that the curve is first conve and then again convex toward the temperature axis, w diate points of inflexion.

In the case of acids and bases, however, and therefo and hydroxide-ion, the rate of increase of the equival steadily decreases with rising temperature, so that the concave toward the temperature axis. With the tri-io other hand, the rate of increase steadily increases, owing crease in the equivalent conductance of the bivalent ion; t fore always convex toward the temperature axis.

It is of interest to note that the fluidity, or the recip cosity, of water shows nearly the same increase as the co di-ionic salts, at any rate up to 156°, which is about th previous determinations of the viscosity have extende for the viscosity (η) the data of Thorpe and Rodger and taking the mean values of Λ_0 for the five uni-univale in this research, the product $\eta\Lambda_0$ has the values 1.19 at 1 and 1.01 at 156°. When it is considered that the co

[1] This Journal, 28, 572 (1906).

[2] With respect to this last temperature-interval sodium acetate

[3] See Landolt-Börnstein-Meyerhoffer, Physikalisch-chemische From the data there given the viscosity in dynes per sq. cm. is fou to be 0.01052 at 18°, 0.00283 at 100°, and 0.001785 at 156°. The for the salts referred to are 113 at 18°, 369 at 100°, and 566 at 156°; t were potassium, sodium and ammonium chlorides, sodium acetat

increase five-fold, this variation in the ratio will be seen to be of secondary significance.

With respect to the variation of the equivalent conductance (Λ) with the concentration (C), it has been found that between the concentrations 0.1 and 0.002 or 0.0005 normal the results of all temperatures with all the salts, both di-ionic and tri-ionic, and also with hydrochloric acid, nitric acid, and sodium hydroxide, are expressed by the function $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$ provided that to the exponent n a value (varying with the different substances) between 1.40 and 1.55 is assigned. This is clearly shown by the summary of the n values given in Table 4. These were

TABLE 4.—VALUES OF THE EXPONENT n IN THE FUNCTION $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$.

Substance.	18°.	100°.	156°.	218°.	281°.	306°.
KCl	1.42	1.40	1.40	1.48	1.50	1.48
NaCl	1.42	1.48	1.50	1.50	1.47	1.46
$AgNO_3$	1.53	1.52	1.50	1.50	1.52	1.52
$NaC_2H_3O_2$	1.45	1.45	1.42	1.36	..	..
HCl	1.45	1.38	1.40	1.47	..	..
HNO_3	1.43	1.45	1.45	..	..	..
NaOH	1.50	1.50	1.50	..	..	..
$Ba(OH)_2$	1.55	1.45	1.45	..	..	..
K_2SO_4	1.42	1.42	1.42	1.42	1.42	1.42
$Ba(NO_3)_2$	1.50	1.50	1.50	1.50	1.50	1.50
$MgSO_4$	1.43	..	..	..	..	..

derived by a graphical method (which involved no assumption in regard to the value of Λ_0), this being regarded as a third constant to be determined from the data themselves. In general, the value of n could be found within 0.02 or 0.03 units.

It is evident that, if the conductance-ratio Λ/Λ_0 can be taken as a measure of the ionization (γ), the latter changes with the concentration in the case of all these substances in accordance with an entirely similar exponential law, namely, in accordance with the function $\frac{(C\gamma)^n}{C(1-\gamma)} = \text{const.}$, in which n has values varying with different substances only between 1.40 and 1.55.

In a previous article[1] emphasis was laid on the remarkable fact that at ordinary temperatures the form of the functional relation between ionization and concentration is the same for salts of different ionic types. These results show that this is also true at high temperatures, and, moreover, that even the very large variation of temperature here involved and the large consequent change in the character of the solvent affect

[1] Noyes, "The Physical Properties of Aqueous Salt Solutions in Relation to the Ionic Theory," Congress of Arts and Science, St. Louis Exposition, 4, 317 (1904); Technology Quarterly, 17, 300 (1904); Science, 20, 582 (1904); abstract in Z. physik. Chem., 52, 635.

only slightly, if at all, the value of the exponent in this relation. Thus an additional confirmation is given tc conclusion that the form of the concentration-function of the number of ions into which the salt dissociates. show almost conclusively that chemical mass-action ha: influence in determining the equilibrium between the i ionized part of largely dissociated substances. How co: tradiction with the mass-action law is, is seen when it is di-ionic and tri-ionic salts this law requires that the conc un-ionized substance be proportional to the square and cu of the concentration of the ions, while the experimental it is proportional to the 3/2 power of that concentratior be the type of salt.

It has been found by trial that the functions Λ_0- $\Lambda_0 - \Lambda = K(C\Lambda)^{\frac{1}{2}}$, which contain only two arbitrary const also satisfactorily express the results with potassium c chloride, hydrochloric acid, and sodium hydroxide at any between the concentrations of 0.1 and 0.002 or 0.0005 1 however, the data at still smaller concentrations, as Kohlrausch and others at 18°, do not conform to the these functions, they apparently do not give by extrap value of Λ_0, and correspondingly the ratio Λ/Λ_0 derived f a true measure of the ionization. It has therefore nc while to make a study of the applicability of these the substances investigated.

The equivalent conductance and ionization of the sligl stances, acetic acid and ammonium hydroxide, on the oth with the concentration at all temperatures, even up to ance with the mass-action law. It is interesting to note acid, an acid of moderate ionization (60 per cent. at 18° at 156° at 0.01 normal concentration), has intermediate 1.9), which, however, approach more nearly the theore than the empirical one.

In order to show the relations between degree of ioniza ter of the substances, and the temperature, the perce of all the substances investigated at the different temp and 0.01 normal solution is shown in Table 5. The su ranged in the order in which the ionization at 18° decrea in the caes of sulphuric acid show the percentage of the which exists in the form of hyrogen-ion, without referen arises through the primary dissociation into H^+ and HSO ary one into H^+ and $SO_4^=$; the values are only approxima an estimate of the relative extent to which these two sta

TABLE 5.—PERCENTAGE IONIZATION.

Substance.	Concentration.	18°.		100°.		156°.		218°		281°.		306°.	
		0.01.	0.08.	0.01.	0.08.	0.01.	0.08.	0.01	0.08.	0.01.	0.08.	0.01.	0.08.
HCl	0.01	97.1	...	95.0	...	93.6	...	92.2	...	..	..	82	...
	0.08	...	93.2	...	89.7	...	87.2	...	82.5	..	..	..	60
HNO_3	0.01	96.8	...	95.2	...	93.4	...	...	...	..	..	..	...
	0.08	...	92.6	...	89.0	...	85.3	...	75	..	..	..	33
NaOH	0.01	96.2	...	95.7	...	94.3	...	92	...	..	..	..	...
KCl	0.01	94.2	...	91.1	...	89.7	...	89.8	...	87	..	81	...
	0.08	...	87.3	...	82 6	...	79.7	...	77.3	..	72	..	64
NaCl	0.01	93.6	...	92.7	...	92.1	...	90.2	...	84	..	80	...
	0 08	...	85.7	...	83.2	...	81.2	...	77.7	..	69	..	63
NH_4Cl	0.01	93.7	...	92.2	...	91.2	...	90.1	...	..	..	79	...
$AgNO_3$	0.01	93.3	...	91.8	...	88.8	...	86.3	..	82	..	77	...
	0.08	...	83.3	..	80.2	...	75.8	...	70.8	..	64	..	57
$NH_4C_2H_3O_2$	0.01	91.9	...	88.7	...	87.1	...	...	...	..	..	..	...
$NaC_2H_3O_2$	0.01	91.2	...	88.8	...	88.0	...	82.2	...	..	..	76	...
	0.08	..	81.1	..	77.6	...	75.6	...	68.5	..	..	..	...
$Ba(OH)_2$	0.01	93	...	85	...	85	...	...	...	..	..	..	...
	0.08	...	83	..	70	...	65	...	...	..	..	..	...
K_2SO_4	0.01	87.2	...	80.3	...	75	...	63	...	47	..	37	...
	0.08	...	73.2	..	64.8	...	58	...	45	..	31	..	23
$Ba(NO_3)_2$	0.01	86.7	...	83.6	...	80	...	74	...	59	..	47	...
	0.08	...	70.1	..	66.9	...	62	...	53	..	38	..	...
H_2SO_4	0.01	83	...	56	...	49	...	46	...	..	..	..	...
	0.08	...	66	..	48	...	45	...	42	..	..	..	35
$MgSO_4$	0.01	66.7	...	52.4	...	35	...	13	...	..	..	..	...
	0.08	...	45.5	..	31.9	...	19	...	7	..	..	..	...
H_3PO_4	0.01	60	...	42	...	29.4	...	...	...	..	..	..	...
	0.08	...	31	..	19.5	...	12.5	...	...	..	..	..	...
$HC_2H_3O_2$	0.01	4.17	...	3.24	...	2.26	...	1.26	...	..	..	..	...
	0.08	...	1.50	..	1.17	...	0.82	...	0.46	..	..	..	0.14
NH_4OH	0.01	4.05	...	3.59	...	2.46	...	1.36	...	..	..	..	...
	0.08								0.47				0.11

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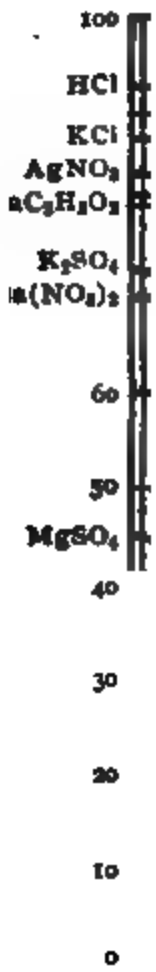

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Thus the rate of decrease in ionization is small between 18° and 100° for either type of salt; but it becomes greater at the higher temperatures, especially in the case of the tri-ionic salts; and for the highest temperature interval (281°–306°) it is extremely rapid for both types of salt. The decrease in ionization of hydrochloric acid, nitric acid up to 156°, and sodium hydroxide is about the same as that of the di-ionic salts; thus the average value of $(-10^3 \Delta\gamma/\Delta t)$ at 0.08 normal for hydrochloric and nitric acids is 0.38 between 18° and 100°, 0.63 between 100° and 156°; and for hydrochloric acid 0.76 between 156° and 218°. Between 156° and 306° nitric acid decreases in ionization much more than the other substances of the same type.

The physical property of the solvent which is most closely related to its ionizing power is, as has been shown by Thomson and Nernst, its dielectric constant. It is, therefore, of some interest to compare its variation with the temperature with that of the ionization of salts. Unfortunately, the dielectric constant of water has been determined only between 0° and 76°. Drude[1] has, however, derived for this interval a quadratic equation, from which a value at 100° may be calculated, probably without great error. The values of the dielectric constant obtained from this equation are 81.3 at 18° and 58.1 at 100°, and the ratios of these is 1.40.

The question now arises, what function of the ionization should be compared with this? It seems clear that, from a theoretical standpoint, it is simplest to consider the ratio $\frac{C_2(1-\gamma_2)}{C_1(1-\gamma_1)}$ of the concentrations of un-ionized salt which prevail in solutions that at the two temperatures (t_2 and t_1) have the same concentration of the ions (that is, solutions for which $C_2\gamma_2 = C_1\gamma_1$); for in such solutions the electric force between the ions, and therefore their tendency to unite to form un-ionized molecules, in so far as this has an electrical origin, must be inversely proportional to the dielectric constant. The above ratio is evidently equivalent, since $C_2\gamma_2 = C_1\gamma_1$ to the ratio $\frac{(1-\gamma_2)/\gamma_1}{(1-\gamma_1)/\gamma_2}$, where, however, γ_1 and γ_2 refer to the slightly different concentrations C_1 and C_2 (C_2 being equal to $C_1\gamma_1/\gamma_2$).

Now for the four uni-univalent salts given in Table 5 the mean values of the percentage ionization at 0.08 normal is 84.4 at 18° and 80.9 at 100°, or by interpolation, 80.6 at 100° at 0.08 × 1.042 normal (that is, at $C_1\gamma_1/\gamma_2$), whence the value of the ratio just referred to is found to be 1.30. The value of the corresponding ratio for the two tri-ionic salts at 0.08 normal is in the same way found to be 1.38.[2] While the former

[1] Wied. Ann. Phys., 59, 50 (1896).

[2] The mean value of the percentage ionization for these two salts at 0.08 normal are 71.7 at 18° and 65.8 at 100°, or by interpolation 64.8 at 100° at 0.08 × 1.09 normal.

f these values differs considerably from the ratio (1.40) of the dielectric onstants, yet all the values lie in the same neighborhood. Indeed, the greement is as close as could be expected, considering the character of ne data involved.

Finally, even though it seems theoretically to correspond to a less comarable condition in the solution, yet, in view of the valence principle edssdisc just below, it is of interest to note the values of the simpler atio, $\frac{C(1-\gamma_2)}{C(1-\gamma_1)}$, of the concentration of the un-ionized substance at two emperatures at the same total concentration, instead of the same iononcentration. At 0.08 the value of this ratio for 100°/18° is 1.22 for he four uni-univalent, and 1.21 for the two uni-bivalent salts, thus conderably less than the ratio of the dielectric constants.

The degree of ionization of the different substances may be next condered in relation to the ionic type to which they belong and to their hemical nature. It has already been pointed out that even up to the ighest temperatures neutral salts of the same ionic type have roughly ne same percentage ionization, the differences not exceeding 8 per cent. n any case investigated. The strong acids, hydrochloric acid and (up o 156°) nitric acid, and the strong bases, sodium and barium hydroxides, lso conform in a general way to this principle, though their ionization eems to be several per cent. greater than that of the corresponding alts; it is worthy of mention, however, that this greater value may be ue to an increase in the equivalent conductance of the hydrogen-ion or ydroxide-ion with the concentration of the solute, as is indicated to be ne case by the transference results which have been obtained with these cids.[1]

It is also remarkable that the rough proportionality which had preiously been shown to exist at ordinary temperatures[2] between the unnized fraction of a salt at any concentration and the product of the alences of its ions has now been proved to persist up to the highest temeratures, where the degree of ionization has become much less. This shown by the following summary: Under A are given the mean values the percentage of un-ionized salt $100(1-\gamma)$, for the neutral salts of each

		18°.		100°.		156°.		218°.		261°.		306°.	
$\nu_1 \nu_2$.	Mols. per liter.	A.	B.	A.	B.	A.	B.	A.	[illegible]	A.	B.	A.	B.
1 × 1	0.04	12	12	15	15	17	17	20	20	25	25	31	31
1 × 1	0.08	15	15	18	18	21	21	25	25	31	31	39	39
1 × 2	0.04	28	14	34	17	40	20	51	25	65	32	74	37
2 × 2	0.04	55	14	68	17	81	20	93	23	..	..	..	..

[1] See This Journal.

[2] For a discussion of this principle, see the author's article on "The Physical Properties of Aqueous Salt Solutions," *Loc. cit.*

type at the concentration 0.04 molal and for the uni-univalent salts at 0.08 molal; and under B are given the ratios of these values to the product of the valences (v_1v_2) of the ions.

It will be seen that the principle continues to hold, especially when the comparison is made at the same equivalent concentration, even when the ionization has become very small; thus it is only 26 per cent. for the uni-bivalent salts at 306° and only 7 per cent. for the bi-bivalent salt (magnesium sulphate at 218°).

The ionization tendencies of phosphoric acid, acetic acid, and ammonium hydroxide, and the effect of temperature on them are best shown by the summary of their ionization-constants which is given in Table 7.[1] The concentration involved in the constant is expressed in equivalents per liter, and the constants themselves have been multiplied by 10^6.

TABLE 7.—IONIZATION-CONSTANTS OF PHOSPHORIC ACID, ACETIC ACID, AND AMMONIUM HYDROXIDE.

Temperature.	Phosphoric acid.	Acetic acid.	Ammonium hydroxide.
0	...	..	13.9
18	10400	18.2	17.2
25	9400	..	18.0
50	7000	..	18.1
75	4800	..	16.4
100	3400	11.1	13.5
125	..	..	10.4
128	2230	..	..
156	1420	5.42	6.28
218	..	1.72	1.80
306	..	0.139	0.093

It is evident from these results that the ionization-constant for ammonium hydroxide increases considerably in passing from 0° to 18°, then remains nearly constant up to 50°, and finally decreases with increasing rapidity as higher temperatures are reached, attaining at 306°, a value which is only about one two-hundredth of that at 18°; and that at all temperatures the values for acetic acid are not very different from those for ammonium hydroxide. Phosphoric acid is seen to have a much larger ionization, which, however, decreases steadily and very rapidly with rising temperature.

The interpretation of the results obtained with sulphuric acid is complicated by the fact that the ionization doubtless takes place in two stages; but in the original publication[2] a method has been described which can only be referred to here, by which it is possible to determine

[1] In the case of phosphoric acid the values vary considerably with the concentration in correspondence with the fact that the exponent in the concentration-function was found to be 1.8–1.9 instead of 2 as required by the mass-action law. The values here given are those at the concentration 0.05 formula-weights (H_3PO_4) per liter.

[2] Publication No. 63 of the Carnegie Institution, p. 271.

he hydrogen-ion concentration within fairly narrow limits from the con-
.uctance alone, without knowledge of the extent to which the separate
tages occur. The method is of general application to dibasic acids,
.nd, if the ionization-constant for the first hydrogen be known, as is true
vith many of the organic acids, the method could be used for computing
hat of the second hydrogen from the conductance at high dilutions
vhere the second ionization is appreciable. The ratio of the hydrogen-
on to the total hydrogen in the case of sulphuric acid is thus found to
'ary in 0.08 normal solution from about 66 per cent. at 18° to 48 at 100°
nd 35 at 306°.

Similar calculations of the hydrogen-ion concentrations have been
nade in the case of potassium hydrogen sulphate. These show that in
.1 molal solution, at 156°, the hydrogen-ion concentration is not more
han 3 per cent.; and this justifies the conclusion that the secondary
onization of sulphuric acid (into hydrogen-ion and sulphate-ion) in its
wn moderately concentrated solutions is also insignificant at this tem-
erature and higher temperatures. Interpreted with the help of this
onclusion the conductivity data for the acid show that the primary dis-
ociation (into hydrogen-ion and hydrosulphate-ion) is about the same
s that of hydrochloric acid at temperatures between 100° and 306°; and
. is reasonable to suppose that the same is true at lower temperatures
own to 18°.

With the help of this principle the ionization of the hydrosulphate-ion
t 18°, 100°, and 156° in the solutions both of the acid and acid salt
as been computed. This ionization is thus found to be large at 18°,
ut it decreases very rapidly with the temperature. Thus in a 0.1 molal
otassium hydrogen sulphate solution equal quantities of sulphate-ion
nd hydrosulphate-ion are present at 18°, while at 100° there is only 15
er cent., and at 156° only 4 per cent., as much sulphate-ion as hydrosul-
hate-ion in the solution.

Only rough values of the ionization-constant of hydrosulphate-ion
nto hydrogen-ion and sulphate-ion can be given, since they vary very
nuch with the concentration; some idea of its magnitude is furnished
y the following values which hold at about 0.01 molal (or 0.002 molal
t 156°): 18500×10^{-8} at 18°, 1220×10^{-8} at 100°, and 115×10^{-8}
t 156°, whereas the ionization-constant of acetic acid at 18° is $18 \times$
0^{-8}. From the change of the ionization-constant with the temperature,
he heat absorbed (ΔE) by the reaction $HSO_4^- = H^+ + SO_4^=$ has been
ound to be given by the expression: $\Delta E = 14{,}170 - 65\,T$, where T repre-
ents the absolute temperature. From this it follows that the value
t 18° is −4750 calories, and at 100° —10,070 calories, while from Thom-
en's heat-of-neutralization measurements and our ionization data at
8° the value —5020 calories is derived.

Conclusion.

In the preceding paragraphs have been summarized the generalizations to be drawn from the results of these investigations, in regard to the behavior of the varous types of chemical substances in aqueous solutions through a wide range of temperature. In conclusion, it seems, however, desirable to draw attention again to a theoretical principle of even more general import, which has been already presented in a previous article by the author as a conclusion apparently justified by a study of the then existing data, for this principle has now received a further confirmation through the demonstration of the fact that certain purely empirical laws relating to the ionization of salts in water still continue to be valid, even when the physical condition of that solvent is greatly altered by a large change in its temperature. This principle is that the ionization of salts, strong acids, and bases is a phenomenon primarily determined not by specific chemical affinities, but by electrical forces arising from the charges on the ions; that it is not affected (except in a secondary degree) by chemical mass action, but is regulated by certain general, comparatively simple laws, fairly well established empirically, but of unknown theoretical significance; and that, therefore, it is a phenomenon quite distinct in almost all its respects from the phenomenon of dissociation ordinarily exhibited by chemical substances, including that of the ionization of *weak* acids and bases.

The most important facts leading to this conclusion are the approximate identity of the ionization values for salts of the same ionic type; the existence of a simple approximate relation between the value of the un-ionized fraction and the product of the valences of the ions; the smal effect of temperature on the ionization of salts and a parallelism between the magnitude of that effect and the effect upon the dielectric constant of water; the validity of an exponential relation between ionization and concentration, which differs from that required by the mass action law, and which is approximately the same at all temperatures and for different ionic types of salts; and the fact that the optical properties and other similar properties of dissolved salts (when referred to equal molal quantities) is independent of this concentration and therefore of their ionization, so long as the solution is even moderately dilute.

The molecular explanation of these facts and the more general conclusions drawn from them would seem to be that primarily the ions are united somewhat loosely in virtue of their electrical attraction to form molecules, the constituents of which still retain their electric charges and therefore, to a great extent, their characteristic power of producing optical effects and such other effects as are not dependent on their existence as separate aggregates. Secondly, the ions may unite in a more intimate way to form ordinary uncharged molecules, whose constituents have com-

pletely lost their identity and original characteristics. These two kinds of molecules may be designated electrical molecules and chemical molecules, respectively, in correspondence with the character of the forces which are assumed to give rise to them. Now in the case of salts and most of the inorganic acids and bases, the tendency to form chemical molecules is comparatively slight, so that the neutral electrical molecules greatly predominate. On the other hand, in the case of most of the organic acids, the tendency to form chemical molecules is very much greater, so that as a rule these predominate. The facts, moreover, indicate that chemical molecules are formed from the ions in accordance with the principle of mass action,[1] but that electrical molecules are formed in accordance with an entirely distinct principle, whose theoretical basis is not understood.

It is to be expected that with neither class of substances will the predominating type of molecule be alone present; and that minor deviations from the mass action law in the case of moderately ionized substances, and from the usual empirical law in the case of largely ionized substances, may well arise from the presence of a small proportion of molecules of the other type. In the former case, we may indeed with some confidence predict quantitatively that that proportion of electrical molecules will always be present which corresponds for the type of substance in question to the concentration of its ions in the solution.

A fuller experimental investigation of the properties of dissolved salts, especially of those of polyionic types, and of the phenomena of the solubility effect and the distribution into a gaseous or another liquid phase of ionizing substances, if combined with a thorough and persistent study of all the available data, gives promise of suggesting a fuller theoretical explanation of this remarkable behavior of largely ionized substances in aqueous solution. Even if such a theoretical interpretation should not be discovered, one may at least hope to determine with greater accuracy and certainty the laws of the equilibrium between the ions and un-ionized molecules, and between the two forms of the latter, in case their existence shall be more fully substantiated. The facts already known make it almost certain that we have here to deal with a new kind of equilibrium phenomenon, and not simply with some deviation of a secondary nature,

[1] The best evidence of this is that furnished by the change of the conductance of slightly ionized electrolytes with the concentration; but distribution experiments also indicate it. Thus it is probable that as a rule the chemical molecules alone distribute into the gaseous phase or into organic solvents and that therefore the concentration of the substance in such phases is a measure of the concentration of those molecules in the aqueous solution; and the few experiments thus far published indicate that the latter is at least approximately proportional to the product of the concentrations of the ions. (Compare the experiments on picric acid by Rothmund and Drucker, Z. physik. Chem., 46, 826 (1903)).

arising, for example, from a somewhat abnormal osmotic pressure, or a change in the migration velocities of the ions, as has been assumed by most authors.

In conclusion, I desire to express to the authorities of the Carnegie Institution my great indebtedness for the assistance rendered me in the prosecution of these researches; for without such aid little progress could have been made up to the present time.

BOSTON, December, 1907.

[CONTRIBUTION FROM THE LABORATORY OF THE MALLINCKRODT CHEMICAL WORKS.]

THE REFRACTIVE INDICES OF ALCOHOL-WATER MIXTURES.[1]

BY LAUNCELOT W. ANDREWS.

Received January 15, 1908.

To Leach and Lythgoe belong the credit of having first determined, by means of the Zeiss immersion refractometer, the refractive powers of aqueous solutions of methyl and ethyl alcohols and of publishing the results[2] in tabular form for the entire range from zero per cent. to one hundred per cent. for the temperature of 20°. An earler table[3] by B. Wagner comprises the range for ethyl alcohol only from zero to three hundred and thirty, expressed in grams per liter.

The method used by the first-named authors for fixing the concentration of the solutions of which they observed the refraction, is not mentioned in their publication, but the inference is that they deduced the concentrations from density determinations by means of Hehner's tables.

Since, in case of nearly absolute and of very strong alcohol, the refractometer and density constants bear such a relation to one another that the concentration may be much more accurately inferred from the former than from the latter, it follows, that the refraction constants should be fixed independently of observations of specific gravity. For this and other reasons, I decided to prepare absolute alcohol, and from this to make, by dilution with known weights[4] of water, the solutions needed for the refractometric work.

Preparation of the Absolute Alcohol.

Three methods came into consideration for the preparation of the absolute alcohol required, *viz.*, the usual quick-lime process; the method of Winkler[5] with metallic calcium, and the Evans and Fetsch[6] and Konek[7]

[1] Read before the American Chemical Society, January 2, 1908.

[2] This Journal, 27, 964 (1905).

[3] Dissertation, Jena (1903).

[4] The weighings were not reduced to vacuum.

[5] Ber., 38, 3612 (1905).

[6] This Journal, 26, 1158 (1904).

[7] Ber., 39, 2263 (1906).

process with magnesium amalgam. It was decided to operate by all three methods and to compare the refractive indices of the products.

The plan contemplated the continuance or repetition of each process until no further change occurred in the constants, and was carried out in that way. Two criteria of complete hydration were made use of, first, the constancy of the refractive index, which falls rapidly as the last portions of the water are extracted, second, the constancy of the critical temperature of solution. The latter method, devised by Crismer,[1] cannot be too highly recommended. It consists, as is well known, in cooling a mixture of equal volumes of the alcohol and of kerosene until the mixture becomes turbid, a sign of the critical temperature having been reached, and observation of the temperature. It was found advisable to free the kerosene from its more volatile constituents by passing a current of steam through it for some time, after which it was dried. This treatment obviated the appearance of a preliminary haze before the critical temperature was reached, a phenomenon that slightly diminished the sharpness of the observations. The following table shows the relation between the C. T. S. (critical temperature of solution) and the percentage of alcohol, as found for the kerosene used by me. It may be seen that if the temperature be read to 0.1°, a difference of 0.005 per cent. in the amount of water present may be easily detected, a fact previously demonstrated by Crismer. With proper precautions, a much closer temperature determination may be secured, but is hardly necessary.

TABLE I.

Per cent. of water.	Per cent. of alcohol.	C. T. S. kerosene.	Diff. per cent. for 1° C.
0.0	100.0	4.0°	0.050
0.2	99.8	8.0°	54
0.4	99.6	11.6°	57
0.6	99.4	15.1°	59
0.8	99.2	18.4°	60
1.0	99.0	21.7°	0.061
0.2	98.8	24.9°	64
0.4	98.6	28.0°	66
0.6	98.4	31.1°	69
0.8	98.2	34.0°	72
2.0	98.0	36.8°	0.075
0.2	97.8	39.4°	77
0.4	97.6	42.0°	83
0.6	97.4	44.4°	91
0.8	97.2	46.6°	0.100
3.0	97.0	48.6°	

The raw material employed for the preparation was that commercially known as "double Cologne spirit." This was digested for three

[1] "Les temperatures critiques de dissolution," Bruxelles (1904).

veeks, being frequently stirred, with good quicklime, and then distilled, he first and last tenths being rejected. To the intermediate fraction, which contained about 99 per cent. of alcohol, silver nitrate was added[1] n the proportion of about five grams to each liter and the solution boiled for about eight hours, under reflux condensation and exclusion of moist air. Then, after standing cold for two or three days, it vas distilled. The distillate contained about 0.3 per cent. of water. Io reaction for aldehydes could be obtained from it. Various portions f this intermediate product were used for the further dehydration with, irst, fresh lime from marble, second, turnings of metallic calcium, third, nagnesium amalgam.

It soon appeared that a too prolonged treatment with either of the last-amed reagents gave an alcohol which, on distillation, was less dry judged by the C. T. S.) than that secured by a briefer treatment. The rue explanation of this deportment is uncertain, although it would be ot difficult to suggest an hypothetical one. The proper period of digesion is shown by the appearance of a pale yellowish tint throughout the quid. When this point is distinctly reached, no matter which of the rying agents be used, if the alcohol is distilled with the usual precauions,[2] the following phenomena were observed.

The first portion of the distillate contained a little water and had a . T. S. (with the standard kerosene referred to above) of about 6°. After pproximately ten per cent. had distilled off, in each case the C. T. S. ose to 4° or 4.15° and remained at that point till nearly all had come ver. In some instances, especially when magnesium amalgam was resent in the distilling vessel, the C. T. S. fell again toward the close of he distillation. Hence, the middle portion alone was used for the deerminations. It may be remarked, however, that the first fraction tenth) was not distinguishable in density from the middle one. In everal instances, the intermediate fraction was subjected a second and third time to the action of the same desiccating agent as before, but n no case was it possible to reduce the C. T. S. below 4° or to obtain a roduct of which the density or refractive index pointed to greater dehyration than that of the 4° material.

It was repeatedly observed that the alcohol dehydrated by prolonged

[1] Winkler, Ber., 38, 3612 (1905).

[2] The remark of Winkler (*Loc. cit.*), that the hygroscopic character of absolute lcohol "has been exaggerated" should not be interpreted in the sense that any preautions to exclude moist air may safely be neglected. This author must have been avored with exceptionally dry atmospheric conditions, or the remark quoted would ever have been made. I can fully confirm the observations of Crismer (*Loc. cit.*, p. 7) n the rapid absorption of water by dry alcohol on exposure to humid air and have not een able under the conditions of my experiments to confirm the divergent observations f Winkler.

contact with either calcium or with magnesium amalgam possessed a peculiar foreign odor, which persisted even after dilution with a little water. The nature of the substance giving this odor is entirely unknown, but its presence does not appreciably influence either of the constants determined. Its amount is, therefore, probably, extremely minute.

The desiccation with calcium or with magnesium amalgam may be effected by contact at the ordinary temperature for several days or at the boiling point of alcohol in half an hour or two hours. The amalgam was prepared by agitating magnesium powder with its own weight of mercury under the surface of 98 per cent. alcohol, acidified with a little hydrochloric acid. When etched in this manner, the mercury soon flows over the surface of the magnesium particles. The alcoholic acid is poured off and the magma washed with absolute alcohol. Other methods of preparation were experimented with, but this was found most efficient and has the advantage of rendering a greater amount of magnesium available in proportion to the mercury.

Apparatus.

The refractometer used was a Zeiss instrument of the immersion type. Its scale was subject to a small correction (—0.24°) which was determined by a series of observations on pure water at 25°. All the readings presented in this paper have been so corrected.

The thermostat used in the work was kept at 25° ± 0.6°. Its temperature never varied more than 0.05° during an observation and very rarely by so much. Each sample of alcohol was observed at least five times after the temperature of the thermostat was attained, and the mean of the concordant readings taken. This mean was corrected for 25° by the temperature coefficient given in Table II.

Two thermometers were used. One was divided in 1/5° and had divisions wide enough to enable 0.01° to be estimated with considerable accuracy. This thermometer was made by Geissler Nachfolger in 1880 of unknown glass. The second thermometer was made of Jena normal glass, divided into 1/10° and read to 0.01°. In order to insure taking the readings on a rising meniscus, in case of all definitive observations the thermometer was removed from the thermostat, waved in the air a moment to cool it about 1° and then replaced.

Fixed points were determined for both instruments at 0° and at the transition point of sodium sulphate (after Richards). The intermediate scale was calibrated by two mercury threads and the reading corrected accordingly and reduced to the international or hydrogen scale by the table of Marck.[1]

With these corrections applied, the two instruments agreed, on direct comparison, for temperatures between 20° and 30° within the limits of

[1] Landolt and Bernstein Tabellen, 44.

the observation errors. A third thermometer was used for some of the density determinations. It was fused into one of the pycnometers. It was compared with the others by filling the pycnometer with mercury and immersing the whole in a mercury bath containing the other instruments and placed in the thermostat.

Two pycnometers were employed, one of about 50 cc. of the Sprengel type, the other of 35 cc. with fused-in thermometer. The errors of a density determination of alcohol amounted to about two units of the fifth place of decimals. It is hardly possible to secure greater accuracy on a liquid of this kind with pycnometers so small as this. The determination of density was not, however, a main object of this investigation.

To obtain a degree of precision in the measurement of this constant commensurate with present means of obtaining pure absolute alcohol, pycnometers or sinkers of not less than 250 cc. should be used.

In all these determinations, except as previously noted, correction to vacuum was made for weights and substances weighed, and the errors of the weights were corrected.

Experimental.

1. Absolute alcohol made by the quicklime method gave C. T. S. 3.9°. Density $^{25°}_{4°}$ 0.785103, 0.785087, 0.785107. C. T. S. after each density determination, 4.1°, 4.1°, 4.0°. Refractometer, mean of 7 observations, 85.30°. Another preparation of the same gave: refractometer readings, mean of 5, 85.33°. C. T. S. 4.15°. Density $^{25°}_{4°}$ 0.785111.

2. Absolute alcohol made by calcium method, digested at about 35°, gave C. T. S. 4.05°. Density $^{25°}_{4°}$ 0.785091, 0.785112, 0.785108. Refractometer, mean of ten readings, 85.29°. A second preparation, made at the boiling-point of alcohol: C. T. S. 3.9°. Density $^{25°}_{4°}$ 0.785105. A third preparation, made with an alcohol from another source, dried in the same manner: C. T. S. 4.1°; refractometer, mean of 5, 85.32°.

3. Absolute alcohol made by cold magnesium amalgam process gave: C. T. S. 4.18°. Density $^{25°}_{4°}$ 0.785102, 0.785110, 0.785095; refractometer, mean of six, 85.35°.

A second lot of the same, but digested hot: C. T. S. 4.03°. Density $^{25°}_{4°}$ 0.785091, 0.785105, 0.785106; refractometer, mean of five observations, 85.30°.

A third preparation, made like the last: C. T. S. 3.95°. Density $^{25°}_{4°}$ 0.785085; refractometer, 85.28°.

4. Total mean of all observations on absolute alcohol:

Density, 0.78510 $\pm$ 0.00001, $^{25°}_{4°}$. Refractometer (weighted mean) 85.30° $\pm$ 0.02 Z, 25°. Index of refraction (μ_D) against air, 1.359408 $\pm$ 0.00001, 25°. Refractive power, $\frac{n_D-1}{d} = 0.45833$; $\frac{\mu_D-1}{d} = 0.45779$.

,. From the absolute alcohol, a series of dilutions with distilled water re made by weighing, at intervals of about two per cent., except in neighborhood of absolute alcohol, where the intervals were closer. ch of these dilute alcohols was observed with the refractometer, at st five observations being taken at each dilution. Subsequently ther dilutions, about ten in all, were made from different prepara- ns. These observations were reduced by a graphic method and in- endently by a series of quadratic equations, which were found to fit various parts of the curve closely. The plotting served as a check the mathematical work and to detect clerical errors in the computa ns. In this manner the scale readings and the refractive indices given the following table were separately computed as they appear in Table When completed, no individual point observed was found to differ

TABLE II.—REFRACTION INDICES AND SCALE READINGS OF THE IMMERSION REFRACTOMETER FOR AQUEOUS ALCOHOLS.

% H_2O.	$\mu_{25°}$	Diff	Zeiss Deg	Diff	Δz for 5° C.
0	1 35941	.	85 30°	..	5 55
1	984—	43 0	86 49°	1.19	5 57
2	6024	40 0	87 60°	1 11	5 59
3	061	36 9	88 63°	1.03	5 61
4	094+	33 8	89 58°	0 95	5 63
5	125	30 7	90 45°	0 87	5 64
6	153 —	27 7	91 23°	0 78	5 65
7	178 —	25 0	91 93°	0 70	5 65
8	200 +	22 5	92 55°	0 62	5 66
9	221	20 3	93.10°	0 55	5 67
10	239	18 1	93 59°	0 49	5 67
11	255	15 9	94 03°	0 44	5.65
12	269 —	13 8	94 42°	0 39	5 62
13	280+	11 9	94 76°	0 34	5 60
14	290	9 6	95 05°	0 29	5 57
15	297 +	7 5	95 29°	0 24	5 55
16	305	7 3	95 49°	0 20	5 52
17	312 —	7 1	95 68°	0 19	5 49
18	319	7 1	95 88	0 20	5 46
19	326—	6 8	96 07°	0 19	5 42
20	331—	5 2	96 22°	0 15	5 38
ix. 20 7	1,363,315	0 5	96.24°	...	...
21	3,313		96 23°	....	5 34
22	3,302	1 2	96 20°	0 03	5 30
23	3,286	1 6	96 16°	0 04	5 26
24	3,265	2 1	96 10	0 06	5.23
25	3,239	2 6	96 03°	0 07	5.20
26	3,208	3 1	95 94°	0 09	5.17
					5 06
30	3,038	.	95 47°	. .	....

NOTE. The percentages of water in the first column are by weight. The r tive indices are against air (μ) The temperatures are given in terms of the inte

national (hydrogen) scale. The figures of the last column give approximately only the differences of the scale readings between 20° and 25°. They may be used for calculating the corrections when the temperature differs by one or two degrees from 25°. The readings presupposed adjustment to read 13.63° in water at 25°. Practically the use of the table is restricted to alcohols stronger than 88 per cent. by weight.

from the corresponding value of the table by an amount larger than could be accounted for by an error in the temperature of 0.03° and in the averaged refractometer reading of 0.04°, and the mean difference was less than half this amount. It is of course possible, and probable, that there are constant errors of greater magnitude. In these, as in previous determinations of the same sort, there is no direct proof that the alcohol may not have contained traces of higher alcohols sufficient to affect the results appreciably, though this seems unlikely. Further, it is not known what may be the magnitude of the errors in the Zeiss table of the relation of the refractometer degrees and the corresponding refractive indices.

The observations show the existence of a maximum of the refractive index at 20.7 per cent. of water. This corresponds very accurately, perhaps by accident, with a hydrate of the composition represented by the formula $3C_2H_6O.2H_2O$. It is very unlikely that the position of this maximum is incorrectly located by a larger amount than 0.3 per cent.

The view has recently found expression that improvements in the technique of making absolute alcohol have reduced the densities found for this substance from the figures obtained by Mendeléeff to those of recent authors. That this view is incorrect is shown by the fact that Crismer obtained exactly the same density numbers as Mendeléeff, although he used the critical temperature of solution method for determining when his alcohol was dry, and this is without doubt the most searching criterion for the purpose yet employed.

The results of Mendeléeff and of Crismer, $D\,{}^{25°}_{4°} = 0.78522$ are given in terms of the mercury-glass thermometer, those of Winkler, Konek, Klason and Norlin, and of the present writer, in terms of the hydrogen thermometer.

Since we do not know the expansion curve for the glass of the thermometers employed by Mendeléeff or by Crismer, it is impossible to say exactly what the difference is. We may, however, assume, with probably a very small error, that the correction to be applied at 25° is 0.11° or —0.000095 on the density. Applying this to Mendeléeff's figure, we have for the density reduced to the international standard, 0.78512. Morley[1] has recently recalculated Mendeléeff's table in part, reducing the densities to the hydrogen temperature standard and he finds for absolute alcohol, at ${}^{22°}_{4°}$, 0.78763. This corresponds to 0.78508 at 25°.

[1] This Journal, 26, 1185.

therefore appears that the absolute alcohol of Mendeléeff was just e and free from water as that obtained by the most modern methods.

Summary.

is demonstrated that the absolute alcohol, prepared by the use of ed marble and freed from aldehydes, has the same density, the same tive index and the same critical temperature of solution as that has been dried by the use of magnesium amalgam or of metallic cal-

: observations of Crismer, to the effect that the critical tempera- f solution of alcohol in kerosene is the best criterion of the dryness olute alcohol, is fully confirmed.

olute alcohol was found to have the following constants:

isity $^{25°}_{4°}$ 0.78510 ± 0.00001.

s immersion refractometer, 85.30° ± 0.02 at 25° H.

ex of refraction (μ) against air, 1.35941 ± 0.00001 at 25° H.

ractive power $\frac{n_D-1}{d}$ = 0.45833; $\frac{\mu_D-1}{d}$ = 0.45779.

able is presented of the refractive indices against air and of the re- meter readings of aqueous alcohols for each per cent. of water o to 30, accompanied by an approximate table of temperature coeffi- of refraction through the same range.

existence is demonstrated of a maximum refractive index of 15 at 25° for the mixture containing 20.7 per cent. of water and er cent. of alcohol, a composition which very closely corresponds ance or otherwise, with the formula $3C_2H_6O.2H_2O$ (calculated, per cent.).

LOUIS, MISSOURI.

IBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY. No. 149.]

WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. THE DETERMINATION OF THE MOLECULAR WEIGHTS AND CRITICAL TEMPERATURES OF LIQUIDS BY THE AID OF DROP WEIGHTS.[1]

BY J. LIVINGSTON R. MORGAN AND RESTON STEVENSON.

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Introduction. Object of the Investigation.

1864, Thomas Tate,[2] as the result of his experiments with water, nced the following laws:

[1] Extract from the Dissertation of Reston Stevenson. Our thanks are due to Higgins for kind assistance in the latter part of the work.

[2] Phil. Mag., 4th Ser., 27, 176 (1864). All other references to drop weight will d in the bibliography of that subject at the end of this paper.

I. Other things being the same, the weight of a drop of liquid (falling from a tube) is proportional to the diameter of the tube in which it is formed.

II. The weight of the drop is in proportion to the weight which would be raised in that tube by capillary action.

III. The weight of a drop of liquid, other things being the same, is diminished by an augmentation of temperature.

Tate's experiments were all made with thin-walled glass tubing, varying in diameter from 0.1 to 0.7 of an inch, the orifice in each case being ground to "a sharp edge, so that the tube at the part in contact with the liquid might be regarded as indefinitely thin." His weights were calculated from the weight of from five to ten drops of liquid, which formed at intervals of 40 seconds, and were collected in a weighed beaker.

Tate's Law, as we know it to-day, is supposed to be a summation of the first two laws of Tate, but it must be said that it attributes to Tate a meaning that he never indicated, and probably never intended. The analytical expression of this faulty law is the familiar

$$W = 2\pi r\gamma,$$

where W is the weight of the falling drop, r the radius of the tube on which it forms, and γ is the surface tension of the liquid. Of course, Tate's second law shows drop weight to be *proportional* to surface tension, for the weight of a liquid rising in a tube by capillary action is proportional to surface tension; and his first law shows drop weight to be *proportional* to the diameter (or radius) of the tube; but he did not even imply that drop weight is equal to the product of the circumference of contact into the surface tension. The real analytical expression of Tate's first two laws, as he actually announced them, in place of the above, should be

$$W = K_1\gamma D,$$

where K_1 is a constant, and D is the diameter of the tube; or, when the drops are all formed on the same tube (*i. e.*, where D is constant),

$$W = K\gamma,$$

K being a new constant.

The general result of the work of all other investigators since the time of Tate, on the subject of drop weight, may be summed up best, perhaps, in the words of Guye and Perrot (1903), *viz.*:

"The law of the proportionality of the weight of a drop to the diameter of the tube is no more generally justified than that of the proportionality of the weight to the surface tension."

"The laws of Tate are not general laws, and, even in the case of static (slowly forming) drops, represent only a first approximation."

It will be seen from these conclusions that Guye and Perrot repudiate not only the form of Tate's law as we know it to-day, but also his first

wo laws in the form that he announced them. It must be said, however, at no investigator has as yet fairly tested Tate's laws, for no one has as yet actly reproduced Tate's conditions. Practically all the results thus r obtained have been for drops forming on capillary, instead of on thin-alled tubes; and the effect produced by the "sharp edge" of the drop-ng tube, as described by Tate, has never been even approximately ap-oached, except under such conditions that the results were obscured r other factors (Ollivier, Antonow).

The object of this investigation, which was started by one of us, six ars ago, is to test the truth of Tate's law (and especially the second), he originally stated them, more fairly and with greater accuracy than s hitherto been done, reproducing his conditions in a way that others ve failed to do, paying particular attention to the effect of the form of e tip, and excluding those errors which are so apparent in the work some of the previous investigators. And it was hoped that even if te's laws were found *not* to hold rigidly, it might still be possible to em-oy the temperature coefficient of drop weight of any one liqiud, in a rmula similar to that of Ramsay and Shields,[1] in place of their tempera-re coëfficient of surface tension, as a means of ascertaining molecular eight in the liquid state, and the critical temperature.

It may be said here, to anticipate, that the results of our work have oven to be even better than we had hoped, for they have shown that t only molecular weights in the liquid state and critical tempera-res, can be calculated just as readily and accurately from the mperature coefficient of drop weight, as from that of surface tension; t also that the relative surface tensions of various liquids can be found om drop weights, and that, thus found, they agree with those termined by the capillary rise as well as do those by any of the her methods, and almost as well as those for the same liquid by the me method, carried out by different observers. This relation to sur-ce tension is true for the interpolated values of surface tension, and rther work, using the actual, experimental values, will probably only ow the relation to be even more rigid than this.

Apparatus and Method.

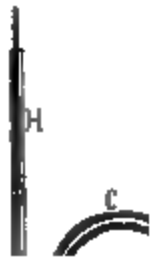
In order to avoid the complication which might be introduced by the cessive formation of several drops, we have measured, throughout r work, *the volume of a single drop*, for that method, under these condi-ons, is far more accurate and delicate than any weighing method.

Although, unlike Tate, we have used capillary tips upon which the op forms, we have so constructed them that we might expect to ob-in an effect similar to that obtained by Tate with the "sharp edge"

[1] Zeit. f. phys. Chem., 12, 431 (1893).

of his thin-walled tube. Apparently the effect of this "sharp edge" is to delimit the area of the tube upon which the drop can hang, and to prevent the liquid rising upon the outer walls of the tube. The form of tip we have employed in our measurements is shown, in section, in Fig. 1(O′), both the bottom and bevel being highly polished.

Observation of a tip of this form shows that it behaves exactly as such a one as described by Tate, and that the lower edge of the bevel, just as Tate's "sharp edge," is the limit of the area upon which the drop hangs, provided, of course, that its diameter is less than that of the maximum drop of the liquid with the smallest maximum drop. *The liquid forming a drop on this tip does not, under any condition, rise to wet the bevel or walls of the tube as it might on an ordinary one.* This effect has also been obtained, during the course of our work, by two other investigators (Antonow and Ollivier), but only by the use of foreign substances, which contaminate the liquid.



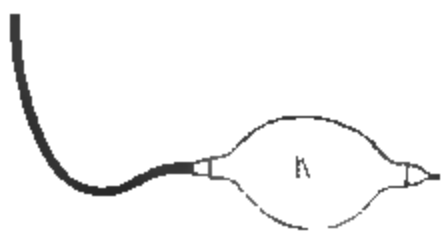


Fig. 1

The complete apparatus used in our preliminary experiments is shown in section, in Fig. 1. *P* is a translucent porcelain scale, 55 centimeters long, divided into millimeters. *AB* is a capillary burette of such a bore that 1 millimeter contains about 0.0003 cc. This tube was carefully calibrated with mercury, and a curve prepared, from which the volume between any two scale readings could be found. One end of this burette, *A*, was connected by rubber tubing to the rubber compression bulb *K*. This bulb was so arranged in a screw clamp that the pressure upon it could be gradually increased or decreased, thus giving absolute and delicate control over the movement of the liquid in the burette. The larger tubing *BC*, which is the continuation of the tip, passes through the

ber stopper R, and thus supports the dropping cup D. F is a dipper ch can be raised, lowered, or swung around to any position by means of rod G. From this the burette can be filled with liquid, and into it the › from the tip O ultimately falls. The bottom of the cup D is covered ı a thin layer of the liquid, and the tube H, through which G passes, is fed with filter paper, saturated with the liquid.

he object of this form of apparatus was to prevent evaporation of the id of the drop, and to enable us to measure drop volumes at any de- d temperature, by immersing the entire apparatus to the point m in aterbath.

efore making a measurement with this apparatus, the cup, dipper, : and tip are thoroughly cleansed with chromic-sulphuric acid, water, hol, and ether, and dried by a current of air. The liquid is then placed he cup and in the dipper, from which, after the stopper R is fastened tly, the tube is filled to such an extent that the lower meniscus is just ut to enter the tip O when the other end of the column (in the burette : AB) is at zero, or some point just below it. This point (*the zero point*) ıen recorded, and the bulb very gradually compressed until the drop ıed at the tip O falls off. The reading of the other end of the column, he instant of fall, then enables one, knowing the zero-point, to find the ıme of the maximum drop that can form on the tip; we shall designate as the *pendant drop* (P. D.). By drawing the liquid, that is left on the back into the tube again, until the lower meniscus is once more just ıt to enter the tip O, it is possible to find the volume of the drop that remained clinging to O; this we shall call the *clinging drop* (C. D.). tracting the volume of this from that of the pendant drop, we finally the volume of the *falling drop* (F. D.).

xperiments with this preliminary apparatus showed the method to be llent, but made apparent the fact that greater delicacy was desirable. second, and final form of apparatus, as shown, in section, in Fig. 2, mply a modification of the first. Here the dropping tube is sealed a glass stopper, and the cup is provided with a wide rim to allow the of mercury as a seal. An elastic band, passed from the hooks Q over stopper, and between the two tubes, holds stopper and cup together. prevents the passage of either mercury or the water of the bath into cup. To obtain a more delicate setting, in determining the zero-point, ı is possible by observing the passage of the meniscus into the tip, dropping tube, here, is constricted at S, and the lower meniscus, in all ings, is held to a mark at that point.

wo pieces of apparatus in this form were used, the burette in one case e 2) holding approximately 0.000,08 cc., and the other (tube 3) 0.000,056

cc. per millimeter.[1] In order that a scale of the same length as before might be used, these measuring tubes were bent in the form shown in Fig. 2. In tube 2 there were three small bulbs blown in the first length of the burette, while tube 3 had a single bulb *V*, with an approximate capacity of 0.027 cc. The use of a bulb or bulbs enabled us to get the total volume of liquid necessary for a drop, without an excessive length of the tubing. For liquids forming drops of large volume, the zero-point must be above the bulb or bulbs; for those giving smaller volumes it must be below the single bulb, or, in case there are three bulbs, below one or more of them.

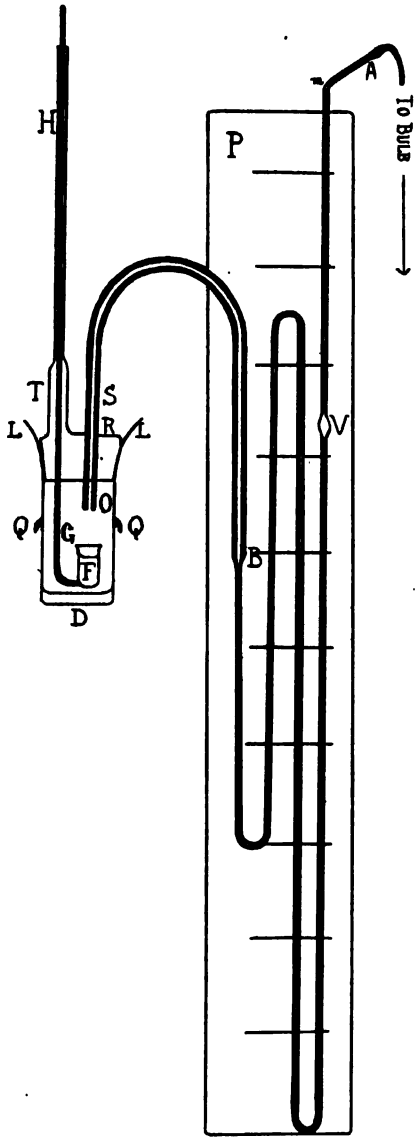


Fig. 2.

With these pieces of apparatus, only the volumes of the falling drops were measured, for the results with the first apparatus showed that, of the three kinds of drops, they only were related to surface tension. Our reason for originally determining the volumes of all three kinds of drops, when Tate considered only the falling drop, was the suggestion of Ostwald[2] that the *pendant drop* from a capillary tube would probably correspond to *falling drop* from a thin-walled tube, such as Tate used. Experiment shows, however, that here, also, the falling drop is the important factor.

To measure the volume of the falling drop with this piece of apparatus, the zero-point is found, just as before, by drawing the liquid back into the burette, until, when the

[1] These tubes were calibrated with mercury at room temperature, and no correction in volume was made when they were used at higher temperatures, for the variations were found to be well within the experimental error.

[2] Hand- und Hilfsbuch zur ausführung Physiko-chemischer Messungen. Leipzig, 1893, pp. 300–301.

r meniscus is at zero or just below it, the lower meniscus is
ly at the mark in the constricted portion of the tube S; then,
efore, the liquid is very gradually forced over until the drop on
tip *O* falls off. No reading for the pendant drop is accepted,
he liquid is at once drawn back to the mark, and, after allowing suffi-
time for drainage, the position of the upper meniscus is observed.
difference in volume of the burette tube, between the zero-point and
atter point, is then the volume of the drop that has fallen. The pres-
on the rubber bulb in all cases must be increased *very* gradually at
nstant when the drop is about to fall, for a sudden increase in pressure
at time tends to increase the volume of the falling drop.

was necessary before using these delicate forms of apparatus to prove
usively that no evaporation takes place from the drop as it is forming
scertain this the tube was filled with liquid, and the zero-point noted
gradually the pressure on the bulb was increased until a large drop
gh not sufficiently large to fall, was formed at *O*. After standing in
condition for several minutes, care being taken, as it must always be
the apparatus was not jarred or disturbed, the liquid is drawn back
the lower meniscus is again at the mark at S. Any decrease in vol
of the liquid, from that originally observed, is then to be attributed
such tips as we have used, to evaporation from the drop. Even our
observations for this purpose, however, showed that there was no
oration, for we invariably found an *increase* in the volume of the liquid
ad of a *decrease*; in other words, liquid was always deposited upon the
ing drop, no matter how often it was formed and drawn back. After
mber of attempts to avoid this deposition upon the forming drop
artially filling the cup with glass beads, sand, or filter paper, moistened
the liquid, and also by the use of a vertically placed bundle of short
d tubes, each filled with the liquid and presenting a meniscus of approx-
nately the diameter of the drop itself, *it was found that it could be*
ed entirely by depositing the liquid (before the experiment) as a fog, upon
alls of the cup D. This fog can be produced very readily by heating
up in a waterbath (after the apparatus has been set up and filled)
to 20°. In this way minute drops of the liquid are deposited upon
walls of the cup, and change the condition within, so that there is then
er evaporation from the hanging drop, nor deposition upon it, and the
r meniscus always returns to the same point, no matter how often
drop may be formed and drawn back. Before each measurement
ssured ourselves, in this way, that such a condition was attained.

will be seen that the delicacy of this method depends simply upon the
of the capillary tubing used as the burette. Tube 3 (1 mm. = 0.000,0
was the smallest tubing available at the time, except, of course, the

very narrow thermometer tubing, which offered too great a resistance to the flow of liquids, for our purposes.[1]

In all cases the apparatus was immersed in a waterbath with transparent sides, the temperature of which was kept constant to the point within 0.1°.

Results.

In Tables I, II, and III are given our results for drop volumes and drop weights, and the relation observed between drop weight and surface ten-

TABLE I.

Diameter of tip = 0.622 cm. approximately. 1 mm. on burtte = 0.0003 cc.

Substance.	Temp.	Surface tension, dynes per cm. γ.	Weights of drop in mgs. $W_{F.D.}$	$W_{F.D.}$	$W_{C.D.}$	Weight of drop / Surface tension $= \frac{W}{\gamma}$ $K_{F.D.}$	$K_{F.D.}$	$K_{C.D.}$
Ether	20.0	16.80	34.6	21.4	13.2	2.06	1.27	0.79
Benzene	22.5	29.38	56.0	35.2	20.6	1.91	1.21	0.71
Ethyl iodide	19.1	30.00	53.2	36.1	17.2	1.77	1.20	0.57
Chlorbenzene	20.0	32.10	66.0	41.4	24.6	2.05	1.30	0.77
Guaiacole[2]	19.6	37.35	78.5	50.0	28.4	2.10	[1.34]	0.76
Benzaldehyde	15.4	39.19	77.3	49.8	27.6	1.97	1.27	0.71
Aniline	17.5	44.10	81.8	52.9	28.7	1.86	1.21	0.65
Quinoline	15.4	45.13	86.6	57.0	29.6	1.92	1.26	0.65
Water	20.0	70.60	127.1	89.1	37.5	1.80	1.26	0.53

Average $K_{F.D.}$ = 1.248±0.012

Mean error of a single result = ±0.035

TABLE II.

Diameter of tip = 0.62 cm. approximately. 1 mm. on burette = 0.00,008 cc.

Substance.	Temp.	Volume of falling drop, cc.	Specific gravity.	Weight of falling drop in mgs. $W_{F.D.}$	Surface tension, dynes per cm. γ	$K_{F.D.} = \frac{W_{F.D.}}{\gamma}$
Benzene	30.5	0.03880	0.867	33.64	26.58	1.260
"	60.7	0.03420	0.833	28.50	22.77	1.251
Chlorbenzene	28.5	0.03561	1.098	39.10	31.02	1.261
"	65.0	0.03220	1.058	34.07	26.91	1.266
Aniline	27.8	0.05033	1.013	50.99	40.69	1.250
"	58.2	0.04675	0.982	45.91	37.32	1.230
Quinoline	28.0	0.04912	1.091	53.58	42.30	1.265
"	65.0	0.04572	1.060	48.47	38.22	1.268
Water	25.5	0.08812	0.9969	87.85	69.70	1.260
"	56.9	0.08180	0.9848	80.55	64.79	1.244
"	79.2	0.07742	0.9722	75.20	60.97	1.233

Average $K_{F.D.}$ = 1.253±0 004

Mean error of a single result = ±0.013

[1] It has since been possible to obtain still smaller tubing, and the work is now being continued in this laboratory with a burette on which 1 millimeter corresponds to about 0.000,046 cc.

[2] Commercial and impure; omitted in computing the average.

TABLE III.

Diameter of tip = 0.62 cm. approximately. 1 mm. of burette = 0.000056 cc.

Substance.	Temp.	Volume of falling drop, cc	Specific gravity.	Weight of falling drop, mgs. $W_{F.D.}$	Surface tension, dynes. γ.	$K_{F.D.} = \frac{W_{F.D.}}{\gamma}$.	$k_{temp.} = \frac{W'_{F.D.}\left(\frac{M}{d'}\right)^{2/3} - W''_{F.D.}\left(\frac{M}{d''}\right)^{2/3}}{t' - t''}$	$k = \frac{\gamma_1\left(\frac{M}{d_1}\right)^{2/3} - \gamma\left(\frac{M}{d_2}\right)^{2/3}}{t_1 - t_2}$ R. & G.	R. & S.
Benzene	22.8	0.03843	0.873	33.55	27.57	1.217	2.600	2.12	2.1043
	73.2	0.03156	0.820	25.88	21.15	1.223			
Chlorbenzene	23.7	0.03519	1.104	38.85	31.68	1.226	2.613	2.10	2.0770
	73.3	0.03032	1.049	31.81	26.04	1.222			
Pyridine	25.5	0.04431	0.976	43.246	35.40	1.221	2.525	2.07	2.226
	72.7	0.03842	0.929	35.692	28.68	1.244			
Aniline	23.0	0.04992	1.018	50.82	41.40	1.228	2.513	2.01	2.053
	71.7	0.04472	0.970	43.38	35.70	1.216			
Quinoline	24.6	0.04810	1.094	52.62	42.67	1.232	2.740	2.21	2.433
	79.7	0.04297	1.049	45.08	36.60	1.231			
					Average,	1.226	2.598	2.105	2.179
					Mean error of average,	±0.0026	±0.041 (1.56%)	±0.033 (1.56%)	±0.07 (3.2%)
					Mean error of single result,	±0.0083	±0.091 (3.5%)	±0.073 (3.49%)	±0.157 (7.2%)

sion, together with the data necessary for the calculations. The surface tensions given, except those for water, are interpolated from the results—determined under the same conditions as our drop weights, *i. e.*, against saturated air—of Renard and Guye,[1] those for water being interpolated from the results of Ramsay and Shields,[2] against the vapor pressure of the liquid. $K_{F.D.}$, $K_{F.D.}$, and $K_{C.D.}$, in Table I, and $K_{F.D.}$ in Tables II and III, are the factors by which the surface tension in dynes must be multiplied to give the drop weight, in milligrams, from these tips. $K_{F.D.}$ is the constant already mentioned in the real analytical expression of Tate's laws, when the same tip is employed. The tips used in Tables I, II, and III, although made from the same tubing, have slightly different diameters exposed, owing to the bevels being cut at slightly different angles. The diameter of the tubing itself was about 6.5 millimeters.

Table I shows our reason for determining the weight of only the falling drop with the more delicate form of apparatus.

In order that errors in our interpolations of the values of surface tension, as well as possible errors in the surface tensions themselves, might not influence our conclusions as to the accuracy of Tate's laws, in Table III, where the determinations are the most accurate, we have also secured a check, without any direct comparison with surface tension, by substituting our drop weights, of the same liquid at two different temperatures, for the surface tensions in the well-known law of Ramsay and Shields, and then comparing the constancy, for the various liquids, of our constant, $k_{temp.}$ with that of those of Ramsay and Shields, ($k_{R.\ \&\ S.}$) and Renard and Guye ($k_{R.\ \&\ G.}$). In other words, for γ in dynes, in the relation

$$\frac{\gamma_1\left(\frac{M}{d_1}\right)^{2/3}-\gamma_2\left(\frac{M}{d_2}\right)^{2/3}}{t_1-t_2}=k=2.12 \text{ ergs,}^3$$

we have substituted $W_{F.D.}$ in milligrams, so that if surface tension (as altered by temperature) and falling drop weight *are* proportional, for any one liquid from the same tip, we should find the expression

$$\frac{W'_{F.D.}\left(\frac{M}{d'}\right)^{2/3}-W''_{F.D.}\left(\frac{M}{d''}\right)^{2/3}}{t'-t''}=k_{temp.}$$

just as constant as the other for all so-called "non-associated" liquids.

All our densities are interpolated from results found in the literature, as were also those of both Ramsay and Shields, and Renard and Guye, so that uniformity in the compared results is thus secured.

All chemicals, with the exception of guaiacol (Table I), which was impure, were specially purified for the purpose.

[1] J. chim. phys., 5, 81 (1907).

[2] Z. physik. Chem., 12, 431 (1893).

[3] M is here the molecular weight as a liquid, d the density, and t the temperature,

Our drop volumes throughout are each the average of several det minations, the extreme variation in tube 3 (Table III) being 0.2–0.4 p cent.

TABLE IV.

Drop weights for various tip diameters. $t = 27°$.

Substance.	$W_{F.D.}$ in mgs. $D_1 = 4.68$ mm.	$D_2 = 6.22$	$D_3 = 7.12$.	$K' = \frac{W_{F.D.}}{D.}$ D_1.	D_2.	D_3.
Benzene.....	26.10	34.60	39 15	5.577	5.563	5.498
Chlorbenzene.....	29.70	40.40	45.10	6.348	6.495	6.190
Quinoline.....	41.15	55.00	62.40	8.792	8.843	8.764

In Table IV are given the drop weights issuing from beveled tips various diameters. These results are not as accurate as some of the othe for tube 2 was used as the burette, and the error in measuring the lo end of the bevel is necessarily large. Under K′ are the values of the co stant of Tate's first law, *i. e.*, weight of falling drop divided by the diam ter of the tip.

TABLE V.

$K_{F.D.} \left(= \frac{W_{F.D.}}{\gamma} \right)$ for tips[1] of various forms.

Substance.	Temp.	Rounded tip. *A* in Fig. 3.	Temp.	Bevel at 30°. *B* in Fig. 3.	Temp.	Sharpened edge. *C* in Fig. 3.	Approximate surface tension
Alcohol.....	58.4	0.907	60.1	1.070	...	...	19
	21.5	0.934	22.5	1.090	21.1	1.123	22
Benzene....	....	.	65.0	1 119	....	. .	21
	....	...	22.1	1.127	....	...	29
Chlorbenzene	64.0	0.932	67.9	1.109	...		27
	22.5	0.965	24.0	1.129	22.0	1.145	32
Quinoline...	64 0	0.124	72.0	1.164	....	...	38
	21 0	1.041	22.6	1.189	22.6	1.157	43
Water.....	23.1	1.086	25.5	1.220	21.0	1 155	72
Average.....		0.983±0.025		1.135±0.017		1.145±0.008	

Table V gives the results obtained by use of tips of various forms, b of approximately the same diameter (see Fig. 3). Tip *A*, here, is round at the end, *B* has a bevel at an angle of about 30°, not sufficient to ha

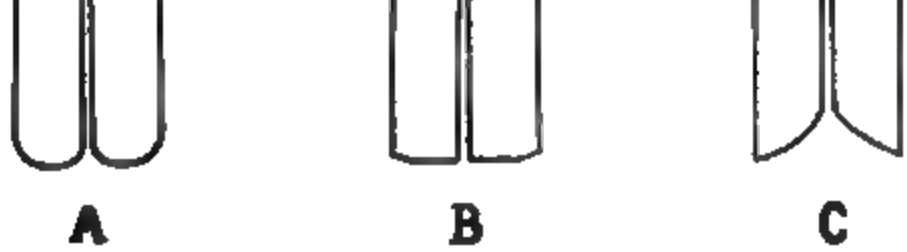


Fig. 3.

[1] Approximately of same diameter.

the effect of a sharp edge, and C, without bevel, has a very sharp edge. All these were measured in tube 2, and consequently the determinations are not as accurate as those in Table III.

TABLE VI.—CRITICAL TEMPERATURES.[1]

Substance.	From $W_{F.D}\left(\frac{M}{d}\right)^{2/3} = k_{temp.}(t-6)$.	From $\gamma\left(\frac{M}{d}\right)^{2/3} = k(\tau-d)$. R. & G.[2]	R. & S.[3]	Observed.
Benzene	286.6	285.8–289.6	288	280.6–296.4
Chlorbenzene	354.1	357.2–358.4	359.7	360.0–362.2
Pyridine	352.0	344.7–346.9	342	.....
Aniline	439.4	448.1–449.1	404.9	425.7
Quinoline	492.3	495.6–496.9	466.1	<520

And, finally, in Table VI, are the critical temperatures of the liquids in Table III, as calculated by the substitution of the drop weight, $W_{F.D.}$, and $k_{temp.}$ for the surface tension γ, and k in the Ramsay and Shields relation,

$$\gamma\left(\frac{M}{d}\right)^{2/3} = (\tau - 6),$$

where τ is the difference between the critical temperature and that of observation, and M, d and k have the same meaning as before.

Discussion of Results.

It will be seen, even from Table I, where the experimental error in drop weight is comparatively large, that, contrary to the conclusion of Guye and Perrot, the relationship between drop weight, *from a properly constructed tip*, and surface tension in saturated air,[4] is very much more than a first approximation, even when the liquids examined include that giving the highest, and that giving almost the lowest, surface tension known, *i. e.*, water at 70.6 and ether at 16.8 dynes per centimeter.

The results in Table II make this conclusion even more striking, for they show that much of the variation in I is due to experimental error. And, finally, Table III, where the accuracy in the determination of drop volume and drop weight was the greatest possible at the time, shows the variation in the constant relationship, for some of the same liquids examined in I and II, to be very small indeed. Here, with five liquids,[5] varying in surface tension from 25.88 to 52.62 dynes, each being studied

[1] Here, in all cases, the temperature coefficient (k or k_{temp}) used is the one found for the specific liquid, and not the average values.

[2] Calculated extremes from surface tensions.

[3] Given by Ramsay and Shields, *Loc. cit.*

[4] According to Renard and Guye, surface tensions in saturated air and those under the vapor pressure of the liquid do not differ by more than 0.5 per cent.

[5] Unfortunately, ether could not be used in either tube 2 or tube 3, owing to interference of a bulb; and the volume of tube 3 was too small to permit water to be used with the beveled tip.

at two temperatures, the mean value of $K_{F.D.}$ for all cases, from a certain tip, is 1.226 ± 0.0026, the mean error of a single result being ±0.0083.

Although in these results the error is small, the discrepancy is still too great—granting the accuracy of the drop weights and surface tensions—to conclude that the proportionality is rigidly exact; even though the agreement is about as good as that observed in results for surface tensions by different methods, and little worse than that shown in the results by any one method, by different observers. The error in drop weight cannot in any case exceed 0.4 per cent., taking all things into consideration, and is generally much less, consequently the discrepancy is only to be explained either by errors in the interpolated surface tensions, or by actual failure of the law of proportionality to hold closer than this (due possibly to a very slight and variable, but unnoticeable, rise of the liquids on the walls of the tip). When it is remembered, however, that the interpolations of the values for surface tension were made from smoothed curves, which could not always be made to pass through all the few points available, it becomes very apparent that in some cases errors in our interpolated surface tensions, even as high as one per cent., are quite possible. If this be true, the law of the proportionality between falling drop weight (from a proper tip) and surface tension becomes rigid. To prove this directly and conclusively has been impossible, for it could be done only by aid of a more delicate apparatus, with measurements of drop weights at the exact temperature at which the surface tensions themselves have been determined.[1] Below, however, it is shown that the interpolated values of surface tension *for any one liquid* are burdened with error, so that analogy would force the conclusion that they, also, are at the root of the error when *different liquids* are considered.

We would conclude, then, from Tables I, II, and III, and from the behavior of tip *C* in Table V, that Tate's second law—the weight of a falling drop (from a proper tip) is proportional to the surface tension (against saturated air) of the liquid—is true. Because surface tensions calculated from drop weights agree, even with those possibly faultily interpolated from results by capillary rise, as well as those determined by other methods agree with these, when directly determined.

Consideration of the columns $k_{temp.}$, $k_{R.\ \&\ G.}$, and $k_{R.\ \&\ S.}$, in Table III, shows that our constants, though calculated from results at only two temperatures, are as constant as those of Renard and Guye, which are in each case the mean of determinations made at several pairs of temperatures and are very much more constant than those of Ramsay and Shields,[2] from

[1] This is now being done in this laboratory.

[2] Although Ramsay and Shields's values were calculated from surface tensions observed under different conditions, their constants are still to be compared with those others as to constancy.

results at two temperatures. It will also be observed that the variation of $k_{\text{temp.}}$ from its mean value is always (when worth considering) in the same direction as that of Renard and Guye's, for the same liquid.

This *certainly proves conclusively that, with any one liquid, from any one tip, drop weight is proportional to the surface tension, as it is altered by changes in temperature, for, by substitution of drop weight for surface tension in the Ramsay and Shields expression, leaving out any direct comparison with the interpolated values of surface tensions, a result is obtained which is as constant as that found by the use of directly determined—not interpolated—surface tensions. And this is true when our interpolated values of surface tension at the two temperatures lead to a discrepancy in the two values of* $K_{\text{F.D.}}$, *as calculated for that liquid. Although this proof is not direct, as far as concerns different liquids, it leaves very little possibility of the slight discrepancy in* $K_{\text{F.D.}}$ *being due to anything but the errors in the interpolated surface tensions as we concluded above.*

We would conclude from the constancy of $k_{\text{temp.}}$, in Table III, then:

That Tate's third law— the weight of a falling drop decreases with increased temperature—is true. And, further, that the change in drop weight for a change in temperature can be calculated accurately *for non-associated liquids*, by the substitution of the drop weight at one temperature for the surface tension, and $k_{\text{temp.}}$ for k in the Ramsay and Shields relation

$$\frac{\gamma_1\left(\frac{M}{d_1}\right)^{2/3}-\gamma_2\left(\frac{M}{d_2}\right)^{2/3}}{t_1-t_2}=k,$$

and solving for the other drop weight.

Or, knowing the drop weights, $k_{\text{temp.}}$, and the densities, it is possible to find the molecular weight of the liquid, with an accuracy equal to that attained when surface tensions are employed directly in the above relation.

Since the molecular temperature coefficient, $k_{\text{temp.}}$, is found to be constant, it is possible, by extrapolation, to find the temperature at which the drop weight would become zero; *i. e., the critical temperature of the liquid*, for at that point the drop would disappear, there being then no distinction between the gas and the liquid. It is only necessary, for this calculation, to substitute $W_{\text{F.D.}}$ for γ and $k_{\text{temp.}}$ for k, in the other form of the Ramsay and Shields relation, *i. e.*,

$$\gamma\left(\frac{M}{d}\right)^{2/3}=k(\tau-6),$$

and solve for the critical temperature (τ plus the temperature at which γ (or $W_{\text{F.D.}}$) is determined). (See Table VI.)

It must be remembered here, however, that in all cases in which we have applied this method, we have done so at a disadvantage, for we have but

two points through which to draw the curve. Further than that we h worked at low temperatures (never above 80°), and consequently w extrapolate from these two points through a much greater distance th either Renard and Guye, or Ramsay and Shields from their larger numbe The first objection holds for all our liquids, though least for benzene b the second hardly affects benzene, for 73.2° is not far from its boiling poi With all high-boiling liquids, both objections hold, and both increase wi the boiling point (and critical temperature).

From the equal constancy of k_{temp} and k, however, it is evident that just accurate critical temperatures can be calculated from drop weights as pr surface tensions, against saturated air, provided in both cases the determinatio from which the molecular temperature coefficients are found, are made as many temperatures, and carried to as high a temperature.

Table IV, it is thought, shows that from such tips, between these di eters, there is a direct proportionality between drop weight and diame of the tip (*Tate's first law*). At least there is no decided trend in the pr portional factor, for it varies just as one might expect it to from the know and fairly large, experimental error. It must be remembered that tip larger than the diameter of the maximum drop would always deliver a *constant* maximum drop weight, while, when the tip becomes small, the is probably a point beyond which the drop will not decrease appreciab in weight for a considerable change in diameter, for it would then b difficult to prevent in any way the rise of liquid upon walls of the tip.

Table V shows that when rounded, a tip behaves differently from the o in Table III; the liquid rises to various heights on the outer walls, and th diameter of the basis for the drop varies with the nature of the liqu This is also true, though to a lesser degree, with the tube that is insuf ciently beveled. In neither case is $K_{p.p.}$ even approximately consta Tip C, on the other hand, compares very favorably with the other bev one, used with Tube 2 (Table II). Whatever theory may be advance then, as to the tip, it will be seen that the point to be considered is th effect of the tip (Tate's "sharp edge") in delimiting the portion up which the drop can hang, especially by preventing the rise of liquid up the walls for that would be variable with different liquids, and lead variable weights. Undoubtedly it is only the failure to follow Tate directions in this respect that has caused the determinations of dr weights, since his time, to negative his conclusions.

Summary.

The results of this investigation may be summarized as follows

1. An apparatus is described by which it is possible to make a very ac rate estimation of the volume of a single drop of liquid falling from a tub and consequently of its weight.

2. With this apparatus was used a capillary tip, beveled at an angle of 45°, which, contrary to those used by other investigators, had the same effect as the one originally used by Tate, *i. e.*, it delimits the area of the tip wetted, by preventing the rise of liquid upon the walls, and thus forces all liquids to drop from one and the same area.

3. It is shown that whenever this effect is obtained, either by use of a properly beveled tube, or one ground to a sharp edge, the drop weight has a different meaning than it has when the drop is formed on either a rounded tip, or on one insufficiently beveled.

4. The falling drop from a capillary tip, and not the pendant drop, is proportional in weight to that of the falling drop from a thin-walled tube with a sharp edge.

5. From such tips as we have used, it is concluded that Tate's second law—the weight of a drop, other things being the same, is proportional to the surface tension (against saturated air) of the liquid—is true.

6. It is shown that from such a tip, Tate's third law—the weight of a drop is decreased by an increase in temperature—is true.

7. Falling drop weights for the same liquid at two temperatures, from such a tip, can be substituted for the surface tensions in the relation of Ramsay and Shields, and molecular weights in the liquid state calculated with an accuracy equal to that possible by aid of surface tensions, under the same, saturated air, conditions. And, by aid of this formula, knowing the molecular weight of a *non-associated liquid*, the falling drop weight at one temperature, and the densities, it is possible to calculate the weight of the drop falling from the same tip at another temperature.

8. Critical temperatures can be calculated by aid of Ramsay and Shields's equation $\gamma\left(\frac{M}{d}\right)^{2/3} = k(\tau - 6)$, by substituting a drop weight for surface tension, and the molecular temperature coefficient of drop weight for k, with the same accuracy attained by the use of surface tensions (against saturated air), provided the drop weights (from which the coefficient is found) are determined at as many temperatures, and at as high a temperature as the surface tensions.

9. For beveled tips, when the diameters lie between 4.68 and 7.12 mm., Tate's first law—the drop weight of any one liquid is proportional, under like conditions, to the diameter of the dropping tube—is true.

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LABORATORY OF PHYSICAL CHEMISTRY.
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THE ACTION OF HYDROGEN SULPHIDE ON ALKALINE SOLUTIONS OF ZINC SALTS.

BY L. W. McCAY.

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The fact that the zinc sulphide, or the zinc hydrosulphide, precipitated rom alkaline solutions of zinc salts by sodium or potassium hydrosulphide s soluble in an excess of these reagents, and that the zinc sulphide, or zinc ıydrosulphide, precipitated from alkaline solutions of the metal by hydro ;en sulphide dissolves when the gas is permitted to act on the solution or some time, appears to have escaped the notice of the analytical chemists. At all events, in no work on analytical chemistry to which I have access s this remarkable behavior of zinc sulphide referred to. The solution o he zinc sulphide is a colloidal one, for the zinc in it will not pass throug parchment paper. The zinc sulphide, or zinc hydrosulphide, acts toward odium and potassium hydrosulphides in much the same way that zinc ıxide, or zinc hydroxide, acts towards sodium and potassium hydroxides The analogy between the two reactions almost compels one to conclud hat the change takes place in the sense of the equation:

$$Zn(SH)_2 + 2RSH = R_2ZnS_2 + 2H_2S.$$

If, however, an alkali sulphozincate is actually formed, it must be ver unstable, for concentrated solutions of mineral salts, when added to it olution, precipitate only zinc sulphide, or possibly zinc hydrosulphide

[1] I noticed this peculiar behavior of zinc sulphide some three or four years ag nd supposed that my observation was a new one. I found, however, that the rea ion was first observed by Julius Thomsen in 1878 (Ber., 11, 2044) and subsequentl xamined by A. Villiers (Compt. rend., 120, 97). Lottermoser (Samlung chem. u ech. Vorträge, VI) und Winsinger (Bull. de l'Acad. des Sciences de Bruxelles, [2] 4, 321) also refer to it.

and then too the zinc sulphide separates out gradually, and in a slimy condition, when the solution is allowed to stand.

In many books on qualitative analysis the student is directed to separate manganese from zinc by adding to the solution of their chlorides an excess of sodium or potassium hydroxide. Now if the alkaline solution of the zinc, after its separation from the manganous hydroxide, be treated for 15–20 minutes with a rapid current of hydrogen sulphide the zinc sulphide which is first precipitated may dissolve. The smaller the amounts of zinc and sodium chloride present in the solution, and the more rapid the current of gas, the more readily does the zinc sulphide formed pass into solution. Should a student pass a rapid current of hydrogen sulphide into such a solution, and then leave the spot and not return until after the lapse of some 15–20 minutes, the chances are he will find the solution clear, or nearly so, and report no zinc. I have convinced myself by a number of experiments that there is, in a case of this sort, considerable danger of overlooking the zinc. It is a significant fact that Fresenius[1] uses hydrogen sulphide water in order to test for the zinc in the alkaline solution. He is also careful to state that an excess of the reagent is to be avoided. However, in describing the special reactions of zinc[2] he states that hydrogen sulphide precipitates from alkaline solutions all the zinc in the form of the hydrated sulphide. Nothing is said about an excess of the reagent, although he does mention the fact that ammonium chloride greatly promotes the separation of the precipitate.

In the following experiments I used a sodium hydroxide solution of zinc oxide containing 8 grams of the oxide in a liter:

1. Ten cc. of the solution were diluted to 150 cc. and treated with a rapid current of hydrogen sulphide. The zinc sulphide was precipitated almost immediately, but at the end of 15 minutes it had passed into solution.

2. To 10 cc. of the solution, made faintly acid with hydrochloric acid, a few drops of a concentrated solution of manganous sulphate were added and the metals precipitated as sulphides with yellow ammonium sulphide. After filtering, dissolving the precipitate in a small amount of very dilute hydrochloric acid, and separating the manganese with excess of sodium hydroxide the alkaline filtrate was diluted to about 150 cc. and treated with a rapid current of hydrogen sulphide. In 15 minutes the zinc sulphide had dissolved and the solution was clear.

3. The experiment was repeated with a solution containing the same amount of zinc oxide along with considerable amounts of manganese, cobalt and nickel. The alkaline solution of the zinc oxide, however, behaved toward the sulphuretted hydrogen gas exactly as it did in 1 and 2.

[1] Anleitung z. qualit. chem. Analyse, 1874, 291.

[2] *Loc. cit.*, p. 137.

On standing, all three solutions became turbid, owing to a gradual separation of the zinc sulphide.

PRINCETON, N. J.,
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THE DETERMINATION OF ANTIMONY AND ARSENIC IN LEAD-ANTIMONY ALLOYS.

BY GEORGE M. HOWARD.

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The separation and determination of antimony and arsenic in alloys with anything like commercial rapidity, and at the same time with a fair degree of accuracy, is by no means a simple matter. The apparent lack of satisfactory published methods led to the development several years ago of the method here described, which, while involving nothing radically new, has proved very serviceable in the author's laboratory.

One great advantage of this method is that tin does not interfere and does not have to be removed, which makes it available for type metal, etc. Iron and copper in small amounts are also without effect, and in fact there seems to be nothing at all likely to be present which interferes. The method is applicable also to many other cases besides lead-antimony alloys—as for instance to the mixed sulphides of antimony and arsenic obtained in many analyses. Some operators object seriously to any method involving the use of hydrogen sulphide, but if the details of manipulation here given are followed there will be no inconvenience whatever from that source.

The procedure is as follows:

The sample in fine filings, 0.5 to 2 grams according to circumstances, is weighed into a 125 cc. Erlenmeyer flask, 60–70 cc. of strong hydrochloric acid added, and two or three drops (not more) of nitric acid (1.4). The flask is then placed on a hot plate where it will be just short of boiling until solution is complete. Frequent agitation considerably hastens the action. It is sometimes necessary to make further additions of nitric acid, but this should be done carefully and an excess avoided. When the metal is all dissolved (10–20 minutes) the flask should be moved where it will boil vigorously for a few minutes until the color changes from reddish yellow to colorless—or, if iron or copper is present, to straw yellow. Now, while still hot, hydrogen sulphide is passed into the solution until it is completely saturated—15 minutes is usually sufficient. If insufficient hydrochloric acid has been used, or the solution has been boiled so long on the plate that much has been lost, antimony sulphide will be precipitated as the solution cools. The hydrogen sulphide treatment is most conveniently handled by fitting the flasks with two-hole

stoppers and inlet and outlet tubes, and connecting several in series to the generator. If the outlet from the last flask is led into a bottle of caustic soda solution, no gas whatever comes off free. When saturated, the flasks are transferred to a current of air, still in series and again absorbing the gas from the last flask in caustic soda, and the air passed until all the hydrogen sulphide is removed (1/2 hour is sufficient for two flasks). The hydrogen sulphide precipitates nothing but arsenic as sulphide, but reduces all salts capable of reduction—antimony, tin, copper, iron, etc. The current of air then reoxidizes all of these except the antimony, which remains in the antimonious form.

To the now cold solution a little tartaric acid is added, and water until its bulk is about doubled, when it is filtered, best through a double filter, into a 16 oz. flask. Practically all of the lead chloride must be washed out of the precipitate with hot water, but it is not necessary to add all the washings to the filtrate, as the antimonious chloride is readily washed out by decantation with cold water.

Antimony.—The filtrate is nearly neutralized by adding powdered sodium carbonate in small portions, care being used not to reach the point of precipitation of the lead, or, if this is reached, making it slightly acid again with hydrochloric acid. The neutralization is then completed with sodium bicarbonate and a slight excess added (about one spoonful of powder). The antimony is then determined by titrating with standard iodine solution, using fresh starch solution as indicator. The precipitate of lead carbonate does not affect the titration, and with a little practice the end point can be recognized just as easily as in a clear solution. Too much starch should be avoided, as it makes the end point obscure. A convenient strength for the iodine solution is 1 cc. = 0.005 gram antimony, then with 0.5 gram samples 1 cc. = 1 per cent. antimony.

If arsenic is negligibly low—which, with a little experience, can be pretty well gauged by the appearance of the precipitate—or for any reason is not to be determined, the filtering may be dispensed with. In this case the whole solution, with the arsenious sulphide, if any, and free sulphur in suspension, is merely transferred to a larger flask, neutralized and titrated. The suspended arsenious sulphide and free sulphur are without effect.

Arsenic.—The bulk of the arsenious sulphide and sulphur is washed off the filter back into the same flask in which the precipitation was made, using not over 20 cc. or so of water. A few drops of sodium hydroxide are added (5 drops of 20 per cent. solution is ample), the solution boiled for a few moments and then decanted through the filter into an 8 oz. Erlenmeyer flask. This weak soda readily dissolves the arsenious sul-

phide, while taking up only a small part of the free sulphur. If the amount of precipitate is at all considerable, it is safer to give a second treatment with soda solution.

The filter is washed with hot water and discarded. To the filtrate is added hydrogen peroxide solution, which should be reasonably fresh or else its strength known. 20 cc. of 3 per cent. solution is sufficient for arsenic up to several per cent. The hydrogen peroxide oxidizes the arsenic and also all sulphur compounds, giving a colorless solution. This is now boiled down to a small bulk, about 20 cc., the excess of peroxide being decomposed in the process. When cool, potassium iodide solution is added in amount equivalent to about 0.1 gram KI, then 20 cc. of strong hydrochloric acid. After standing five minutes it is cooled and titrated with standard thiosulphate, adding three drops of starch solution only when the color is almost gone. A convenient strength for the thiosulphate solution is 1 cc. = 0.001 gram arsenic, and it should, of course, be frequently standardized. It is well also to run a blank titration, using the same amounts of reagents as in the analysis, to determine whether there is any constant to be deducted from the burette reading, due to impurities in the reagents.

The difficulty with the end point experienced by many in this titration appears to be due to using too large an excess of potassium iodide and too much starch. With the proportions given above, the end point is exceedingly sharp, and the reaction seems to be just as complete as when more potassium iodide is used. The heating due to adding the strong hydrochloric acid is sufficient without any digesting, as is sometimes recommended.

After oxidizing and concentrating, the arsenic is in a form to be readily determined in several ways, although the above method is preferred on account of ease and rapidity. For instance, the arsenic may be precipitated with silver nitrate as silver arsenate, after neutralization with acetic acid, and the combined silver titrated with thiocyanate, as in the well known modified Pearce method. In this case care must be used to wash the sulphide free from lead chloride, and also to have all reagents free from chlorine (most of the hydrogen peroxide solutions on the market contain hydrochloric acid). Or, the arsenic may be determined gravimetrically by precipitation as ammonium magnesium arsenate. In this case it is better to use ammonia instead of sodium hydroxide to dissolve the arsenious sulphide.

LABORATORY OF
THE ELECTRIC STORAGE BATTERY CO.,
PHILADELPHIA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, OHIO STATE UNIVERSITY.]

THE INFLUENCE OF TEMPERATURE ON THE ELECTROLYTIC PRECIPITATION OF COPPER FROM NITRIC ACID.[1]

BY JAMES R. WITHROW.

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While determining copper electrolytically with stationary electrodes, it was observed upon several occasions that after the copper appeared to be almost all precipitated it slowly re-dissolved and disappeared from view within a very few minutes. This took place without any change in the current conditions as registered on either the ammeter or voltmeter. Evidently the conditions for the determination were very close to the limits of the ability of the current to precipitate the metal. A slight variation of the conditions, therefore, in some one of the possible directions during the course of an experiment, was sufficient to permit the free nitric acid in the electrolyte to overcome the influence of the current and dissolve what metal had already been deposited.

Increasing temperature of the electrolyte caused by fluctuation of the gas pressure was blamed for the difficulty. It was soon found that higher temperatures than customary[2] existed in the electrolytes which caused trouble. The following work was then undertaken to ascertain just what were the safe limits of temperature for a variety of concentrations of nitric acid, using a fixed amount of current.

Platinum-iridium dishes approximating the customary form were used as cathodes. They were 9 cm. in diameter and 5 cm. deep and when they contained 100 cc. the cathode area was about 100 sq. cm. The anode was a platinum-iridium wire nearly 1.5 mm. in diameter (about No. 15, B. and S. gauge). It was bent in the form of a spiral 4 cm. in diameter, comprising three complete turns. In all, there were 26.5 cm. of the wire exposed to the electrolyte. The current was supplied by storage cells, and the current conditions given in the tables have been calculated to the "Normal Density" from the instrument readings, because the "Normal" cathode surface was not used. The American Instrument Company's Type 2 switchboard ammeter had a capacity of one ampere and the scale was divided into hundredths. The voltmeter had a capacity of 50 volts with scale divisions of half volts.

As a result of some preliminary experiments the distance between the electrodes was maintained at 2 cm. throughout the work. This made their actual separation at all points approximately uniform. The current strength was kept constantly at 0.08 amp. (per 100 sq. cm.). The total dilution was maintained at 125 cc. When nitric acid was added to the electrolyte the metallic deposits were in all cases brilliant and com-

[1] Read at the Chicago meeting of the American Chemical Society.

[2] Edgar F. Smith's "Electrochemical Analysis," 3d Ed., 1902, p. 59.

pact except at the higher temperatures (above 70°). In these latter cases the deposits were not smooth and burnished but were made up of a collection of lustrous individual crystals of copper. When examined under the microscope these crystals were of octahedral aspect. The deposits from the solutions in which nitric acid was entirely absent, were of a different character. All deposits were, however, thoroughly adherent, and no tendency to sponginess was observed in any case. This good condition of the deposits enabled them to be weighed without the use of a drying oven. Washing with boiling water was dispensed with for the same reason.

They were washed thoroughly with distilled water, carrying off the excess with a siphon in the usual manner without breaking the circuit. When washed free from all electrolyte the dish was removed and rinsed with dilute, and then absolute alcohol. Finally absolute ether was used, and after the adhering ether had been all vaporized and the dish rubbed on the outside with a piece of chamois skin it was placed in a desiccator and weighed in from 15 to 30 minutes. The wash water, or at least the first portion of it, was always preserved and tested in the usual manner. When, however, this solution was neutralized with ammonium hydroxide and acetic acid added followed by potassium ferrocyanide the presence of a trace of copper was often observed.

Occasionally, during the progress of the work there was a discoloration of the anode. This discoloration was of a more or less milky appearance, but at times it resembled anodic deposits that have been obtained from the electrolysis of gold solutions.[1] At other times it was like burnished deposits of gold itself. This discoloration was probably of the nature of a deposit for it could be removed by the touch of a finger, or immersion in nitric acid. No increase in weight of the anode could be detected, however, even in several determinations run for upwards of 20 hours. When the deposit was removed by nitric acid no change in the weight of the anode greater than a tenth of a milligram could be detected except in a single isolated case of 0.3 mg. No further attention was therefore given to the matter at this time. The amount of copper considered as present in the solutions used in the work was the mean of several determinations which were run until the electrolyte gave no further tests for copper.

It was found that in the complete absence of nitric acid the copper from a solution of pure copper sulphate (containing 0.25 gram of metal) could be completely precipitated in 16 hours. The rate of precipitation of copper was therefore determined from this electrolyte, in the total absence of nitric acid, to point out the value of the addition of this acid.

[1] This Journal, 28, 1353.

$CuSO_4$. Cu in grams.	HNO_3. cc.	Total dilution. cc.	Current. N.D.$_{100}$ amp.	Current. Volts.	Temp. Centigrade.	Time. Hours.	Cu found. Gram.
0.2503	0	125	0.08	3.3–2.6	25	1	0.1112
0.2503	0	125	0.08	3.3–2.5	25	3	0.2234
0.2503	0	125	0.08	3.3–3.3	25	6	0.2482
0.2503	0	125	0.08	3.3–2.8	25	13	0.2510

In the absence of nitric acid the copper did not appear as rapidly upon closing the circuit as it seemed to do in the presence of small amounts of this acid. In the above determinations the solutions appeared to take on an olive-green tint before the copper became visible. This was also observed when a solution containing only copper nitrate was electrolyzed, but not when free nitric acid had been added. Owing no doubt to the liberation of sulphuric acid, the conductivity of the electrolytes in the above determinations increased steadily, requiring continued increase in the resistance of the rheostat to maintain the current strength at 0.08 ampere per 100 sq. cm. The deposit was about as bright at the end of one hour as it would be from a nitric acid electrolyte. After about two hours, however, the copper began to come down on this bright deposit in a pulverulent form. It would come off as a powder, if touched, but never of its own accord, even upon thorough washing. It appeared velvety and had completely lost its metallic luster. In color it approached the so-called "cherry-red" of powdered hematite. This pulverulent copper was in all cases only a superficial coating, as was shown by treating it with dilute nitric acid, when it dissolved with ease, exposing the bright copper beneath.

The copper from this electrolyte was completely precipitated in 13 hours. The deposit, however, weighed high. This seems to be a common complaint against the sulphuric acid electrolyte, if the determinations are run too long.

The rate of precipitation of the metal was determined from a solution of copper nitrate to which no free acid had been added.

$Cu(NO_3)_2$. Cu in grams.	HNO_3. cc.	Total dilution. cc.	Current. N.D.$_{100}$ amp.	Current. Volts.	Temp. Centigrade.	Time. Hours.	Cu found. Gram.
0.2505	0	125	0.08	2.9–2.5	25	1	0.1087
0.2505	0	125	0.08	2.8–2.6	25	3	0.2208
0.2505	0	125	0.08	2.9–2.6	25	6	0.2450
0.2505	0	125	0.08	2.8–3.7	25	12	0.2504

These deposits were not all like those from pure copper sulphate. They resembled the deposits obtained in the presence of free nitric acid, but were not so brilliant and had a slight tendency to be pulverulent at the center. A comparison of these two tables will show that while the copper may appear first from copper nitrate, yet slightly more is precipitated in a given time after one hour and beyond, from copper sulphate.

Using the copper sulphate solution the rate of precipitation of copper

was determined at 25° in the presence of varying amounts of nitric ac
(sp. gr. 1.42).

$CuSO_4$. Cu in grams.	HNO_3. cc.	Total dilution. cc.	Current. N.D.$_{100}$ amp.	Current. Volts.	Temp. Centigrade.	Time. Hours.	Cu found. Gram.
0 2503	0.25	125	0.08	2.2–2.4	25	1	0.1024
0 2503	0.25	125	0.08	2.2–2.6	25	3	0.2217
0.2503	0.25	125	0.08	2.4–2.6	25	6	0 2445
0.2503	0.25	125	0.08	2.3–2.8	25	12	0 2499
0.2503	0.25	125	0.08	2.3–3.1	25	13	0.2504
0.2503	1.0	125	0.08	2.1–2.2	25	1	0 1060
0.2503	1 0	125	0.08	2.2–2.3	25	2	0.1897
0.2503	1.0	125	0.08	2.2–2.4	25	3	0.2223
0.2503	1.0	125	0.08	2.2	25	6	0.2439
0.2503	1.0	125	0 08	2.2–2 4	25	9	0.2489
0.2503	1.0	125	0.08	2.2	25	12	0.2501
0.2503	1.0	125	0.08	2.2	25	13	0.2503
0 2503	1 0	125	0.08	2.2–2.5	25	15	0 2504
0.2503	1.0	125	0.08	2.0–2.5	25	20	0 2505
0.2503	1.0	125	0.08	2.2–2.4	25	23	0.2503
0.2503	1.0	125	0.08	2.2–2.5	25	24	0.2502
0.2503	1.0	125	0.08	2.2–2 5	25	24	0.2506
0.2503	2.5	125	0.08	2.2–2.3	25	1	0.0916
0.2503	2.5	125	0.08	2 2–2.3	25	3	0.1972
0.2503	2.5	125	0.08	2.0–2.3	25	6	0.2418
0.2503	2.5	125	0.08	2.2	25	13	0 2501
0.2503	2.5	125	0.08	2 2–2.4	25	14	0.2501
0.2503	6.25	125	0.08	2.2–2.3	25	1	0.0512
0.2503	6.25	125	0.08	2.2–2.3	25	3	0.1245
0.2503	6 25	125	0.08	2.2	25	6	0 1585
0.2503	6 25	125	0 08	2.2–2 4	25	13	0.2394
0.2503	6.25	125	0 08	2.2	25	17	0.2414
0.2503	12.5	125	0 08	2.2	25	13	0.0003
0.2503	62.5	125	0.08	1.5	25	2	0.0000

From the results given above it will be seen that the rate of precip
tion in presence of 0.25 cc. of nitric acid was slightly lower than w
no free acid is present in the copper nitrate electrolyte and much lo
than with pure copper sulphate. This gave a fairly good idea of
retarding effect of the presence of nitric acid. The effect, howe
was not great, and the improvement in the character of the depo
more than compensated for it.

In the presence of 1 cc. of nitric acid a quarter gram of copper
precipitated in 12 to 13 hours. Running the determination for 15,
23 or 24 hours had no effect on either the appearance or weight of
deposit. The results in presence of this amount of acid were alm
identical with those from the 0.25 cc. nitric acid electrolyte.

When two per cent. (2.5 cc.) of nitric acid was present the precip
tion of a quarter gram of copper required 13–14 hours. The ret
ing influence of the free nitric acid was now becoming more emph

and when five per cent. (6.25 cc.) of acid was used, the effect was pronounced. In this case the precipitation of the quarter gram of copper was still incomplete after 17 hours. As this was too long an interval for the precipitation of such a small amount of this metal, the work with these conditions was not carried farther. The result with ten per cent. nitric acid (12.5 cc.) came from a faint film (or line) of metal at the upper edge of the cathode surface exposed to the electrolyte, and probably should not be called a deposit from this strength of solution. Red oxides of nitrogen were evolved from the solution containing 50 per cent. nitric acid and no copper was deposited. This work showed that nitric acid retarded the precipitation of copper, but that as it had such a beneficial effect on the character of the deposits, the presence of a small amount was a most desirable addition. The following comparison of the amounts of copper precipitated in six hours from the electrolytes containing varying amounts of free nitric acid, illustrates very clearly the retarding effect of this acid, a fact already appreciated by those who have used this electrolyte.

Electrolyte.	Temperature centigrade.	Cu present. Gram.	Cu deposited in 6 hours. Gram.
$CuSO_4$ + 0 cc. HNO_3	25	0.2503	0.2482
$Cu(NO_3)_2$ + 0 cc. HNO_3	25	0.2505	0.2450
$CuSO_4$ + 0.25 cc. HNO_3	25	0.2503	0.2445
$CuSO_4$ + 1.00 cc. HNO_3	25	0.2503	0.2439
$CuSO_4$ + 2.50 cc. HNO_3	25	0.2503	0.2418
$CuSO_4$ + 6.25 cc. HNO_3	25	0.2503	0.1585

Having found just what the influence of nitric acid was on the precipitation of copper at ordinary temperature, the minimum amount of this acid was used in a number of experiments at higher temperatures.

$CuSO_4$. Cu in grams.	HNO_3. cc.	Total dil. cc.	Current. N.D.$_{100}$ amp.	Current. Volts.	Temp.	Time. Hours.	Cu found. Gram.
0.2503	0.25	125	0.08	2.4–2.3	40°	1	0.0972
0.2503	0.25	125	0.08	2.3–2.4	40°	3	0.2261
0.2503	0.25	125	0.08	2.3–2.4	40°	6	0.2493
0.2503	0.25	125	0.08	2.3–2.5	40°	7	0.2500
0.2503	0.25	125	0.08	2.4–2.4	60°	1	0.0833
0.2503	0.25	125	0.08	2.3–2.2	60°	3	0.2288
0.2503	0.25	125	0.08	2.2–2.3	60°	6	0.2501
0.2503	0.25	125	0.08	2.1–2.1	70°	1	0.0683
0.2503	0.25	125	0.08	2.1–2.1	70°	3	0.2214
0.2503	0.25	125	0.08	2.1–2.2	70°	5	0.2488
0.2503	0.25	125	0.08	2.2–2.3	70°	6	0.2501
0.2503	0.25	125	0.08	2.1–2.1	80°	3	0.1823
0.2503	0.25	125	0.08	1.7	80°	6	0.2491
0.2506	0.25	125	0.08	2.1–2.2	90°	3	0.0821
0.2503	0.25	125	0.08	2.1–2.3	90°	6	0.2460
0.2503	0.25	125	0.08	.....	70°	6	0.0000
0.2506	0.25	125	0.08	2.4–2.2	25–70°	3	0.2258

From these results it seemed that even the slight elevation of perature to 40° decreased the time by a considerable amount. A ther elevation to 60° still decreased the time but to a much smalle tent, while 70° did not seem to improve the results at 60°. In fac time reducing effect of increased temperature reached its limit at 60 and from that point any elevation of temperature had a retarding on the precipitation. This is well illustrated by a comparison o amounts of metal deposited in six hours at the various temperat

Electrolyte.	Temperature.	Cu present. Gram.	Cu deposited hours. Gra
$CuSO_4$+0 25 cc. HNO_3	25°	0.2503	0 2445
$CuSO_4$+0.25 cc. HNO_3	40°	0.2503	0 2493
$CuSO_4$+0.25 cc. HNO_3	60°	0.2503	0.2501
$CuSO_4$+0.25 cc HNO_3	70°	0.2503	0.2501
$CuSO_4$+0.25 cc. HNO_3	80°	0.2513	0.2491
$CuSO_4$+0.25 cc. HNO_3	90°	0 2503	0.2460

Upon one occasion where the current strength had fallen to 0.0 pere and the copper appeared almost all precipitated, the elect was heated with the result that about half of the dish was clean its deposit in spite of the fact that the current increased at the time to 0.15 ampere. That the increased solvent power of nitric with elevated temperature, greatly overbalances the current's inc power of precipitation is further shown in the case of the five per nitric acid electrolyte. At 70° no copper is precipitated, whereas gram is precipitated in the same time at 25°.

In the case of the last determination in the table the temperatur maintained at 25° for two hours and forty-five minutes. It was raised to 70° during the next ten minutes and held there for the re ing five minutes of the three-hour period. The result indicates t celerating influence of increase of temperature, it being much than for the same period of time at either 25° or 70°. This inf of temperature on electrolysis is completely masked at first in all where the electrolyte is heated to the desired temperature before ing on the current. From the table it will be seen that the amo copper precipitated in one hour is less and less as the temperatu creases. After this first hour, however, the beneficial effect of inc temperature is to be seen in every case until the temperature at the solvent action of the nitric acid begins to persistently di the electrolytic deposition.

Conclusions.

1. Even the smallest amounts of nitric acid have a tendency to the electrolytic precipitation of copper, under the conditions here

2. The presence of nitric acid is, nevertheless, desirable beca its beneficial effect on the character of the deposit.

3. While in general increased temperature means accelerated precipitation, yet with the low current strength and conditions here used, the reverse is the case above 70°, no doubt owing to the rapidly increasing solvent action of the acid.

COLUMBUS,
August 7, 1907.

THE GRAVIMETRIC DETERMINATION OF TELLURIUM.

BY VICTOR LENHER AND A. W. HOMBERGER.

Received January 17, 1908.

Of all the methods proposed for the precipitation of tellurium perhaps the one which is most used is a modification of the original method of Berzelius. He used sulphurous acid as a precipitating agent.

The method of procedure as commonly carried out consists in adding to the hydrochloric acid solution of tellurium a strong aqueous solution of sulphur dioxide and allowing this mixture to remain in a warm place for a few days in order to effect a complete precipitation. It has been shown by Schroetter,[1] Brauner,[2] Norris and Fay,[3] Crane,[4] Frerichs,[5] and others that the precipitation by means of sulphur dioxide is far from satisfactory. Brauner has pointed out that part of the precipitated tellurium undergoes oxidation in the liquid, becoming converted into the tetrachloride, in which form it remains in solution. Crane has suggested that the main cause of the incomplete precipitation by means of sulphur dioxide is the very rapid increase in the ratio of the acids to the unprecipitated tellurium in solution, two-thirds of this being due to the hydrochloric acid set free, and one-third to the sulphuric acid formed. He thought if these could be removed the reduction would be complete. The hydrochloric acid could be eliminated by evaporation, but the continuous increase in sulphuric acid would soon interrupt the reaction. This might, however, be kept under control by the addition of sodium or potassium hydroxide.

Whitehead has suggested a remedy in the use of acid sodium sulphite. He advises a moderately concentrated solution of the sulphite and that the quantity added to the tellurium solution be sufficient only to just neutralize the acids present and that formed during the reaction. When the solution is thoroughly agitated and then allowed to stand in a warm place, the precipitate will form and settle evenly. He states that "while acid sodium sulphite does not completely remove all of the tellurium from the solution in the cold, that if not used in great excess and the

[1] Chem. News, **87**, 17.
[2] J. Chem. Soc., **55**, 392.
[3] Am. Chem. J., **20**, 278.
[4] *Ibid.*, **23**, 408.
[5] J. für pr. Chem., **66**, 261.

mixed solutions be raised to the boiling point, toward the end of action the precipitation will be perfect, and the tellurium will be obta in a state of aggregation favorable to easy filtration."

Frerichs has worked on the basis that hydriodic acid and sul dioxide cause immediate and complete separation of tellurium fro tellurous solution even in the cold, and McIvor[1] has confirmed this met

Norris and Fay[2] have demonstrated that under ordinary wor conditions precipitated tellurium increases in weight about 0.5 per c owing to oxidation and that this increase is balanced by the quan of the elements left behind as tellurium tetrachloride in the stro acid solution in which the precipitate is formed by sulphur dioxide. believe that it is more accurate to weigh tellurium dioxide than to w tellurium in the elementary state.

McIvor[3] and Donath[4] have studied the precipitation of tellu by hydrosulphurous acid. This method possesses the disadvan of a precipitate of tellurium contaminated by more or less sulphur. method hardly possesses any advantages over the sulphurous acid cipitation.

Stolba[5] in 1873 and later Kastner[6] have proposed the precipita of tellurium from an alkaline solution by means of grape sugar.

Later, Gutbier[7] described the precipitation of tellurium by mean hydrazine as a method for its determination. His method of proce is to dissolve telluric acid in warm water in a porcelain dish cov with a glass cover and add by means of a pipette a 10 to 20 per c solution of hydrazine hydrate. A dark blue almost black color is n and after heating a short time, elementary tellurium is precipit in a flocculent condition, the liquid becoming colorless. He conti the addition of hydrazine hydrate until the fluid is no longer col by further addition of the reagent.

Experimental.

Precipitation by Hydrazine. -In our hands the method of Gutbier fairly good results. The fact should be noted, however, that the add of an excess of the hydrazine does not at once precipitate all of the lurium. It is preferable to add a small amount of the precipita agent from time to time. This necessitates several hours for comp precipitation. The following results were obtained by Gutbier's me in hydrochloric acid solution:

[1] Chem. News, 87, 163.
[2] Am. Chem. J., 20, 278.
[3] Chem. News, 87, 163.
[4] Z. angew. Chem., 1890, 214.
[5] Z. anal. Chem , 11, 437.
[6] *Ibid.*, 13, 142.
[7] Ber., 34, 2724.

TeO_2. Gram.	Te required. Gram.	Te obtained. Gram.
0.2247	0.1795	0.1790
0.1988	0.1588	0.1577
0.2006	0.1603	0.1596
0.2056	0.1643	0.1637

Precipitation by Sodium Acid Sulphite.—In order to completely precipitate the tellurium by this reagent from a hydrochloric acid solution of a tellurous compound, the solution must contain excess of the reagent and must be allowed to stand in a warm place for twenty-four hours. In the following experiments, the sodium acid sulphite was prepared freshly for this purpose by passing sulphur dioxide into a solution of sodium carbonate. It has been our experience that when acid sodium sulphite which has not been freshly prepared is used for the precipitation of tellurium, the precipitated element frequently contains sulphur.

That it is necessary for the solution to stand a considerable length of time is apparent from the following experiments, all of which experiments were made under exactly the same conditions. The solution of the dioxide in hydrochloric acid was brought to boiling, a saturated solution of acid sodium sulphite was added, the solution allowed to stand the requisite length of time, then brought on a Gooch platinum filter washed with water until the filtrate no longer showed chlorides, after which it was washed with 15 cc. of alcohol and dried at 105°.

	Te required. Gram.	Te obtained. Gram.	Error. Gram.
Solution allowed to stand two hours	0.1609	0.1586	—0.0023
" " " "	0.1609	0.1590	—0.0019
" " " "	0.1767	0.1744	—0.0023
Allowed to stand six hours	0.1609	0.1600	—0.0009
" " "	0.1609	0.1603	—0.0006
" " "	0.1374	0.1366	—0.0008
" " "	0.1527	0.1517	—0.0010
Allowed to stand twenty-four hours	0.1609	0.1615	+0.0006
" " " "	0.1609	0.1618	+0.0009
" " " "	0.1726	0.1730	+0.0004
" " " "	0.1286	0.1289	+0.0003

After tellurium, which has been precipitated by means of sodium sulphite and hydrochloric acid, has been washed thoroughly with water, and alcohol, it oxidizes very slowly when heated as high as 200° as evidenced by the following data:

Length of time of heating.	Temperature.	Te(1).	Te(2).
15 minutes	105°	0.1619	0.1620
15 "	105°	0.1619	0.1620
1 hour	120–130°	0.1620	0.1622
1 "	200°	0.1620	0.1623

Precipitation by Means of Sulphur Dioxide.—By the treatment of tellurium dioxide dissolved in hydrochloric acid with a freshly saturated

solution of sulphur dioxide and allowing to stand for 24 hours, the following results were obtained:

Te required Gram.	Te obtained Gram.
0.1607	0.1617
0.1609	0.1613
0.1609	0.1615
0.1609	0.1613

Unless the acidity in this precipitation is ten per cent., the telluri is not likely to be completely precipitated or it will be precipitated a very fine state of division. The solution should also be hot in or to secure satisfactory precipitation.

Simultaneous Precipitation by Means of Sulphur Dioxide and Hyd zine.—By bringing both sulphur dioxide and hydrazine into a telluri solution the whole of the element is thrown out of the solution alm instantaneously. The solution should have an acidity of 5 to 10 cent. and it is desirable to have the solution in a high degree of conc tration. The solution is brought to boiling and 15 cc. of a satura solution of sulphur dioxide is added, then 10 cc. of a 15 per cent. so tion of hydrazine hydrochloride and again 25 cc. of the sulphur di ide solution. The solution is boiled for a few minutes when the elem tary tellurium will settle in such a way that it can be rapidly wash The precipitate is then transferred to a platinum Gooch filter and wash first with hot water until all of the chlorine is removed, and then w 15 cc. of alcohol. The crucible and contents are then dried at 100-1 and finally weighed.

The following results were obtained by the process as outlined abo using 10 cc. of solutions of hydrazine hydrochloride of different streng with sulphur dioxide. Tellurium dioxide was used for the analy

Strength of hydrazine hydrochloride. Per cent.	Te required Gram.	Te obtained. Gram.	Error Gram.
20	0.1731	0.1735	+0.[illegible]
20	0.2065	0.2068	+0.0003
20	0.1638	0.1641	+0.0003
20	0.1608	0.1608	0.0000
15	0.2212	0.2210	—0.0002
15	0.1435	0.1434	—0.0001
15	0.1605	0.1607	+0.[illegible]
15	0.1072	0.1070	—0.0002
10	9.1658	0.1656	—0.0002
10	0.1642	0.1637	—0.0005
10	0.1268	0.1264	—0.0004
10	0.1422	0.1420	—0.0002

That hydrazine must be there in sufficient quantity is evidenced the following series of tests in which a 6 per cent. solution was used al

with sulphur dioxide and the solution boiled only a few minutes, other conditions being exactly the same as in the preceding series of experiments.

Te required. Gram.	Te obtained. Gram.	Error. Gram.
0.1508	0.1374	—0.0134
0.1701	0.1443	—0.0258
0.1608	0.1535	—0.0073
0.1521	0.1140	—0.0381
0.1903	0.1781	—0.0122

The following two experiments were made with a large excess of sulphur dioxide water along with a 6 per cent. solution of hydrazine and the solution heated six hours.

Te required. Gram.	Te obtained. Gram.	Error. Gram.
0.1680	0.1545	—0.0135
0.1516	0.1416	—0.0100

The method which has been used in this laboratory for a number of years and which has proven the most satisfactory for the gravimetric determination of tellurium is as follows: The tellurium either as derivative of the dioxide or as a tellurate, should be present in a solution which has an acidity of approximately ten per cent. of hydrochloric acid and it is preferable to have the solution sufficiently concentrated, otherwise the fine state of division of the precipitate will render it unsatisfactory for washing. The solution is heated to boiling and 15 cc. of a saturated solution of sulphur dioxide added, then 10 cc. of a 15 per cent. solution of hydrazine hydrochloride, and again 25 cc. of a saturated solution of sulphur dioxide. The boiling is continued until the precipitate settles in such a way that it can be easily washed. This boiling should not take more than five minutes. The precipitated tellurium after being allowed to settle is washed with hot water on a Gooch filter until all of the chlorine is removed, after which the water is displaced by alcohol and the crucible and contents dried at 105°.

UNIVERSITY OF WISCONSIN,
MADISON, WIS.

LOSS OF PHOSPHORIC ACID IN ASHING OF CEREALS.

BY SHERMAN LEAVITT AND J. A. LECLERC

Received December 26, 1907.

Recent work in this laboratory on the determination of phosphoric acid in the ash of wheat has brought to the attention of the writers the fact that whereas the temperature below fusion, at which ashing of grain is carried on, makes very little difference in the percentage of ash, there is a loss in the corresponding values of phosphorus, varying with the temperature.

The fact that there is danger of losing phosphorus where grains are a
wed to become fused during ashing, has been known for some yea
d the methods of the Association of Official Agricultural Chemists f
e determination of phosphoric acid in ash were originated with th
ea in view. In grains rich in phosphorus, such as cottonseed-me
e methods of the A. O. A. C. prescribe charring and extracting the char
ass with acetic acid or water. Many analysts, however, do not consid
necessary to make a previous extraction on a grain comparatively l
phosphorus, such as wheat. Our results show that there is a loss
osphorus below the fusing point of the ash, and, as stated above, th
s varies with the temperature.

The greater part of the phosphorus in wheat is in a water-soluble fo
own as phytin, a substance of relatively high molecular weight co
red to the phosphorus molecule. A comparatively large percenta
the phosphorus may be lost in ashing without appreciably changi
e amount of ash. Two grams of a sample of ground wheat were weigh
to a flat platinum dish and ashed in a muffle at a temperature of l
dness for five hours until the ash was gray or white. The ash was th
ighed and dissolved in a few cubic centimeters of concentrated nitric ac
d filtered and the determination of phosphoric acid made by the vo
etric method of the Association of Official Agricultural Chemists.

It was found rather difficult to produce a perfectly white ash at the te
rature used in the muffle, so a higher temperature was tried and the c
sponding phosphoric acids determined. The substance used in eve
se was wheat ground so as to pass through a one millimeter sieve. T
ies of ashings were carried out, one at low redness, in which the samp
re allowed to heat up from the cold muffle, and the other set ashed
distinct redness.

TABLE I.—AVERAGE RESULTS OF SEVEN SAMPLES DUPLICATED.

Averages.	Ash at low redness.	Ash at redness.	Per cent P_2O_5, low redness.	Per cent. P_2O_5, redness.	Per cent. los P_2O_5.
Seven samples....	2.02	1.99	0.74	0.40	46.0

The results from which Table I was obtained were all determined in dup
te and averaged, and the final table made from these averages. In eve
se the difference in the ash between ashing at redness and at low redn
s less than 0.1 per cent., whereas the loss of phosphoric acid vari
tween 39 and 53 per cent.

As is well known, the addition of calcium acetate prevents the volatili
n of phosphoric acid. Two samples in which the percentage of ph
oric acid had been previously determined by ashing with an excess
cium acetate were then ashed in the ordinary way in the muffle at a co
ratively low temperature, one duplicate of each determination bei
ced in the back part of the muffle and the corresponding ones in t
nt of the muffle.

TABLE II.

Number of sample.	Per cent. P_2O_5 by calcium acetate.	Per cent. P_2O_5. Back of muffle.	Per cent P_2O_5. Front of muffle.	Per cent. P_2O_5 lost. Back of muffle.	Per cent. P_2O_5 lost. Front of muffle.
2154	1.03	0 85	0.97	17.5	5.8
2155	1.05	0.63	0.90	40.0	14.3

We see from Table II that the loss of phosphoric acid is greatest in the back of the muffle where it is hottest and least in the comparatively cool part of the muffle. The loss in either case, however, is an appreciable one and shows the necessity for ashing at a comparatively low temperature.

In order to make a more thorough study of this loss of phosphorus a number of samples were ashed in the regular way at redness; a duplicate set was also ashed by treating with 5 cc. of a solution of calcium acetate of such a strength to furnish more than enough calcium to fix all of the phosphoric acid and render it non-volatile. (A solution yielding about 0.03 grams CaO in 5 cc. of the solution is suitable for 2 grams of grains.) The samples treated with calcium acetate solution were heated on a steam bath to dryness and burnt over the free flame and finally heated for fifteen minutes over the blast lamp and weighed for ash, allowing for the correction of calcium oxide in 5 cc. of the acetate solution. Phosphoric acid was determined in the ordinary way.

Twenty-three samples of wheat gave the following results:

TABLE III.

Per cent. ash at redness.	Per cent. ash, acetate method.	Per cent. loss, ash.	Per cent. P_2O_5 in ash at redness.	Per cent. P_2O_5, acetate method.	Per cent. P_2O_5 lost.
2.09	2.07	1.0	0.64	0.99	35.0

Eighteen of the above samples gave a difference of less than 0.10 per cent. between the ash at redness and the ash by the acetate method. The phosphoric acid varied between 10 and 50 per cent. loss. Table III shows us that there is no appreciable loss of ash but a loss of 35 per cent. of the total phosphorus determined as phosphoric acid.

Samples when ashed at a very low temperature (the dishes radiate a faint glow) for five hours in a muffle, gave practically no loss of P_2O_5. Nineteen samples gave the following results:

TABLE IV.

Ash, ordinary method, low redness.	Per cent. ash, calcium acetate method.	Per cent. loss, ash.	Per cent. P_2O_5, ordinary method	Per cent. P_2O_5, calcium acetate method.	Per cent. loss, P_2O_5.
1.95	1.93	1.0	0.91	0.93	2.0

Thirteen of the above samples varied less than 0.10 per cent. between ash results by the two methods and all of the phosphoric acid results checked within 0.10 per cent. Determination of ash and phosphoric acid are almost identical.

All of our results show that the temperature of ashing below fusion i
ot so important a factor where only the percentage of ash is desired, bu
hen determining the phosphorus as phosphoric acid in ash the greates
ution must be observed to keep the temperature below the volatilizatio
oint of the combined phosphorus.

LABORATORY OF VEGETABLE PHYSIOLOGICAL CHEMISTRY,
BUREAU OF CHEMISTRY,
U. S. DEPARTMENT OF AGRICULTURE.

THE COLORED SALTS OF SCHIFF'S BASES.

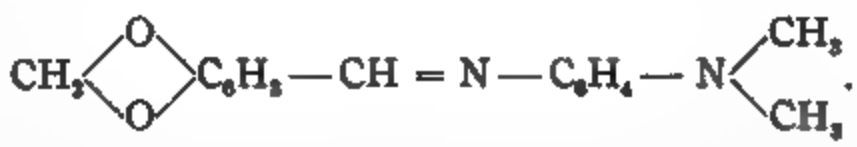
A Contribution to Our Knowledge of Color as Related to Chemical Constitution.

BY F. J. MOORE AND R. D. GALE.

Received January 6, 1908.

The Hydrochlorides of Bases Formed by Condensing *p*-Amino Di methylaniline with Aromatic Aldehydes.

The starting point of the present investigation was a chance observa on made upon the compound produced by condensing *p*-aminodimethy iline with piperonal. This product is of a light orange color and ha e formula

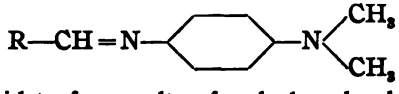


When this substance, either in the dry state or in ethereal or benzen lution, is treated with dry hydrochloric acid gas, one molecule of th tter is first added to form a salt of a deep blood-red color. This sa n further add another molecule of the acid to form a dihydrochlorid he color of the latter salt, in sharp contrast to that of the former, is right lemon-yellow.

We found this phenomenon so striking that we determined to prepa number of compounds of analogous constitution and study the col their salts. The first substances selected were those most strict nalogous to the one already mentioned, namely, the condensation pro cts of *p*-aminodimethylaniline with aromatic aldehydes. These bas rnish the subject matter of the present paper. They all show a b avior toward hydrochloric acid, and (so far as has been tested) al ward other acids, entirely analogous to that described in the case e piperonal compound. A minor exception has to be noted in t se of anisaldehyde. When its condensation product with *p*-amin imethylaniline is treated with hydrochloric acid, the same color chang re observed as in the other cases, but analysis of the products show th maximum of nearly three molecules of the acid is here absorbed. Th ehavior will be discussed more fully in the experimental part.

Subsequent papers will deal with other compounds similarly constituted. Thus we have prepared a number of bases of this class by condensing aromatic aldehydes with *p*-aminodiethylaniline. Of these it may be said that as far as investigated, they show the same reactions toward acids as the corresponding dimethyl compounds. The salts are, however, less stable. One of us, in collaboration with Mr. R. G. Woodbridge, Jr., is also studying the bases formed by condensing *p*-aminodiphenylamine with aldehydes. These bases unite with one molecule of hydrochloric acid to form dark red salts like the monohydrochlorides already described. These salts, however, do not add a second molecule of the acid.

From the above it is clear that we are dealing with a quite general law which may be stated thus: Bases of the general formula



add hydrochloric acid to form salts of a dark red color (darker than that of the free base) while most of them also add another molecule of the acid to form salts of a light yellow color (usually lighter than that of the free base).

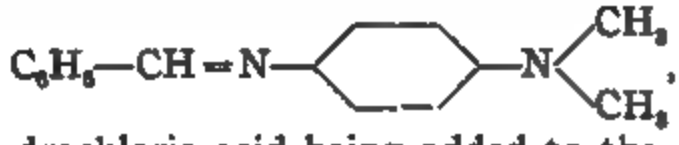
Before attempting a theoretical explanation of this uniform behavior, a word should be said concerning the color of the simpler benzylidene compounds containing only one atom of nitrogen. As aromatic aldehydes condense so readily with primary amines, a voluminous literature has grown up on the subject. We have not made an exhaustive study of this, but the general rule seems to be that neither such bases nor their salts are very highly colored. This certainly holds true of those which have come under our observation. Thus the condensation product of benzaldehyde with aniline is a pale cream color (perhaps due to a trace of impurity) and the product formed by treating piperonal with aniline is perfectly colorless. The hydrochloride of the piperonal compound is a bright lemon-yellow, that of the benzaldehyde compound a much paler shade, only slightly stronger than that of the free base. For purposes of comparison we have prepared several other condensation products of piperonal. All of these, namely the compounds prepared by treating piperonal with *p*-toluidine, *p*-chloraniline, *p*-bromaniline, *p*-aminoethylbenzoate, and *m*-nitraniline, all showed the same light color of base and salt.

From this we can draw the conclusion that if the group —CH = N— is to be considered a chromophore at all, it is a weak one; certainly far weaker than —N = N—. Of the intensifying effect of acid addition or salt formation, whether we call it "auxochrome" effect or "halo-

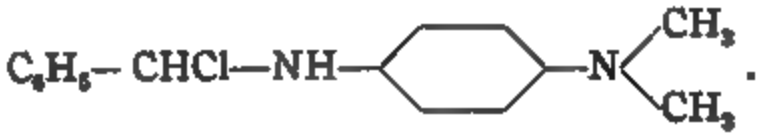
hromy," we may say that in this group of compounds it is noticeabl
ut not striking.

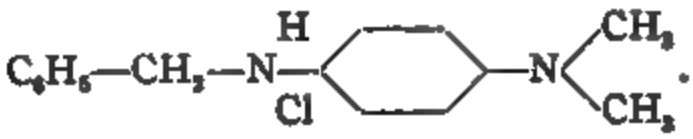
Turning back now to the more complicated bases containing two atom
f nitrogen, inspection of their formulae shows the presence of the sub
tituted amino group, $-N\begin{matrix}CH_3\\CH_3\end{matrix}$, which acts as an auxochrome in s
many important dyes. The effect of this group is seen in the color c
he bases which contain it. These colors range from a light yellow
hrough golden yellow, to a fairly strong orange. None go as far as dee
ed. The color of the salts has already been dwelt upon.

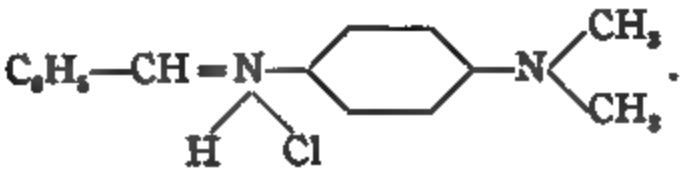
Our interpretation of the color relations so frequently referred to wi
epend upon our idea of exactly what happens when one molecule c
ydrochloric acid is added to these bases. If we take for purposes c
lustration the simplest case, that of benzylidene *p*-aminodimethy
niline,

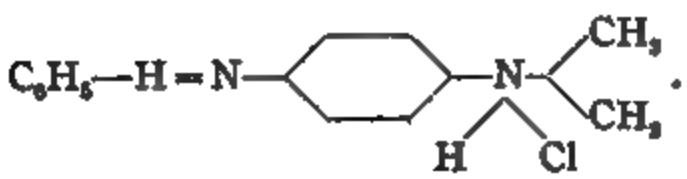


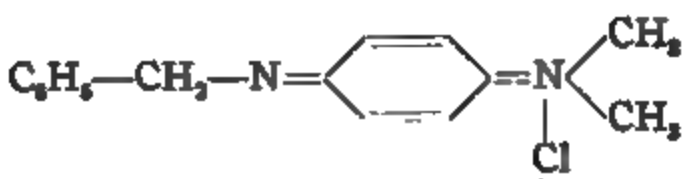
we can imagine hydrochloric acid being added to the compound in su
lifferent ways as to form products of any one of the following formula

(1) 

(2) 

(3) 

(4) 

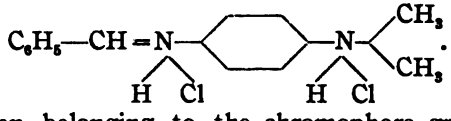
(5) 

Of these, (1) and (2) seem hardly worthy of serious consideration. T
addition products of acids to the simpler bases of this type, such as benz
dene aniline, $C_6H_5-CH=N-C_6H_5$, have always been looked upon
ammonium salts. They split at once under the influence of water in
he corresponding aldehyde and the salt of the base from which th
were originally formed, in this case, aniline hydrochloride and benz
lehyde. The salts of the more complicated compounds now under d

cussion act in a similar way. This would exclude (1). It would not necessarily exclude (2), according to which the addition products are to be looked upon as secondary chloramines. They are, however, rather more stable than chloramines would be expected to be, and they do not evolve chlorine when they are treated with hydrochloric acid. A more conclusive argument, however, against (1) and (2), and in favor of the salt-like character of the compounds is the fact that so far as tested (and only qualitative tests have thus far been made) sulphuric acid gives addition products entirely similar in color and properties to those formed by hydrochloric acid.

Formulae (3) and (4) represent more nearly what we should expect if the addition of hydrochloric acid is to be looked upon as simple salt formation. The formulae differ only in the nitrogen atom, which is supposed to become pentavalent. In deciding between them we have to remember that the simpler bases like piperonylidene aniline add one molecule of hydrochloric acid to form salts which are not dark red but light yellow. Now these salts must have their hydrochloric acid united to that nitrogen which forms part of the chain connecting the two benzene rings. It would therefore seem quite probable that these red salts have their hydrochloric acid bound differently. Furthermore, if we assign to the red salt the formula (4), a consistent and plausible explanation lies near at hand for the difference in color between the salts containing one and two molecules of hydrochloric acid respectively. In the first case, we have three factors coöperating to intensify the color, the chromophore group, —CH=N—, the auxochrome group, $N\begin{matrix}CH_3\\CH_3\end{matrix}$, and, finally, whatever influence in this direction is to be ascribed to salt formation—"halochromy."

Now the compound with two molecules of hydrochloric acid can hardly have any other formula than the following:



Here the nitrogen belonging to the chromophore group, —CH=N—, has changed its valence, and this might naturally be expected to prove destructive to the chromophore character of the group. Furthermore, the light yellow color of these saturated salts is in entire harmony with the similar color of the simpler bases which, as already pointed out, must have the hydrochloric acid upon the central nitrogen.

An argument against the explanation just outlined might be found in the hydrolysis of the salts. It is a well known fact that the salts of the simpler bases like benzylidene aniline decompose at once when treated

with water, yielding, in this case, aniline hydrochloride and benzaldehyde. The salts of the more complicated bases we are studying react similarly except that the operation takes place in two steps. If the yellow hydrochloride of piperonylidene *p*-aminodimethyl aniline, for example, be treated with water, it immediately turns dark red, obviously owing to the formation of the red monohydrochloride. The color then slowly fades out as this salt splits into the hydrochloride of *p*-aminodimethyl aniline and piperonal. Now the weak spot in the hydrochloride of piperonylidene aniline is obviously the molecule of acid attached to the central nitrogen. If the red salt has then a constitution analogous to that shown in formula (4), it is not, at first sight, quite clear why it should hydrolyze at all. The above argument, however, against (4) does not seem as serious as that which can be brought against (3). If we give the latter formula to the red hydrochloride, we can only ascribe the intensity of its color to salt formation—halochromy. We should then expect a further intensification of the color when the second molecule of hydrochloric acid is added. As we have already seen, this is not the case.

There remains the quinoid formula, (5). This also offers a consistent explanation. We have only to assume that the red hydrochloride exists in the quinoid, the yellow dihydrochloride in the benzoid form. It seems at first a little difficult to account for the hydrolysis into aldehyde and amine salt on this basis, but the shifting of double bonds involved is not of a particularly revolutionary character. It would also seem possible that the dihydrochlorides might also exist in a quinoid form. Perhaps, when more compounds have been studied, such salts will be found. In the meantime, some work is under way in this laboratory designed to throw light upon the probability of a quinoid formula for the red hydrochlorides.

An explanation, differing from any of the above, has occurred to us since reading a recent article by Anselmino[1] which came to our notice after the experimental work described in this paper was practically completed. Anselmino found that when *p*-homosalicylic aldehyde is condensed with aniline the product formed exists in two different forms, a red and a yellow. That this is not simply a case of dimorphism is shown by the fact that the two forms differ in chemical behavior and give different derivatives. The most probable assumption concerning their constitution would seem to be that they are stereoisomeric in the same sense as the isomeric oximes of unsymmetrical ketones. If we try to explain the behavior of the compounds we are studying upon a similar basis, we should have to say that the salts vary in color because they are derived from different stereoisomeric bases, one red the other yellow. That i

[1] Ber., 40, 3465 (1907); also *Ibid.*, 38, 3989 (1905).

the case of the bases themselves, the yellow form is alone stable; that when the bases add hydrochloric acid, the yellow salts first formed are unstable and go over to form salts of the other—red base. Finally, when the saturated salts are formed, that a transformation in the opposite sense takes place. This explanation disregards the question as to which nitrogen holds the hydrochloric acid. Now, in this connection, we have to remember that previous to this recent work of Anselmino, no well attested cases of stereoisomerism had been observed among benzylidene compounds, though they have long been looked for; and, further, that Anselmino himself observed no such isomerism in the case of the salts. In fact he points out that his red and yellow bases gave identical hydrochlorides. This, of course, is no conclusive argument against a stereochemical explanation of the facts which we have observed. It does, however, furnish a reason for not accepting such an explanation hastily.

It will be seen in the experimental part of this paper that the salts of salicylidene *p*-aminodimethylaniline undergo change in color on standing, and it has been already pointed out that compounds of this class containing the diethylamino group show similar behavior. From what has already been said, it will be seen in what a variety of directions, an explanation of this fact might be sought. Any discussion of these possibilities would, however, be premature until more work upon these ethyl compounds has been done. For the present also we wish to reserve any opinion as to the probable formulae of the red hydrochlorides.

Experimental Part.

The condensation product of *p*-aminodimethylaniline with benzaldehyde was first prepared by Calm.[1] It is interesting to note his observation that this base adds two molecules of hydrochloric acid to form a "white" salt. This illustates the light color of the saturated hydrochloride, and at the same time shows that Calm attached no significance to the formation of the red intermediate product. He gives a determination of chlorine in the saturated salt. The other bases studied in this paper were prepared by Nuth[2] at the suggestion of Calm. He did not prepare salts. We have little to add to his description of the bases, except for some melting points already corrected by more recent observers. We prepared the bases by mixing molecular quantities of the amine with the various aldehydes, sometimes warming a little on the water bath. The reaction then proceeded at once and gave good yields. The product was recrystallized once from alcohol. It was usually found that further recrystallization did not raise the melting-point. The bases range in color from a light yellow to a light orange.

[1] Ber., 17, 2938 (1884).
[2] *Ibid.*, 18, 573 (1885).

studying the salts, we at first allowed hydrochloric acid to act upon bases in the dry state. When piperonylidene *p*-aminodimethyl- ıe, for example, is spread upon a piece of porcelain (a crucible cover) ı current of hydrochloric acid passed over it, the mass suddenly turns :p red. This color no sooner appears than it begins again to fade g to the formation of the light yellow saturated salt. A similar is produced when the base is dissolved in dry ether and hydrochloric gas introduced. Here the liquid first turns dark red; then a precipitate e same color appears, and, finally, the time varying with the amount bstance present, the color of the solution grows rapidly lighter in :, the precipitate becomes bright yellow, and at the end, the super ıt liquid is colorless, the saturated salt being practically insoluble her. It will frequently be noticed that at the mouth of the tube e the gas enters, and where consequently the acid is always in ex a yellow deposit of the dihydrochloride forms at once. This makes ›bable that the red salt, however it is prepared, contains a good deal e yellow enclosed. This shows itself in the analytical data furnished er on. When the salts were prepared for analysis, the following pro 'e was employed in order to avoid this kind of contamination as ı as possible. First, the free base was dissolved in sodium-dried and then a solution of hydrochloric acid in dry ether was run in a burette. When preparing the saturated salt, the addition of the solution was continued as long as any precipitate formed. To pre an unsaturated salt, a little less than half as much acid was added ıd been found necessary in preparing the saturated one. The pre ıtes so obtained were filtered by suction, washed repeatedly with dry , and finally dried in a vacuum desiccator containing both concen d sulphuric acid and sticks of caustic soda. If lumps formed during rying, these were ground up and the desiccation continued. As far r observation goes, these salts melt only with decomposition, and the erature observed depends largely upon the time of heating. In the of the saturated salts, the point of decomposition lies quite close o° in almost all cases. The chlorine determinations were in all cases by the Carius method. The salts precipitated and dried as above ibed were used for analysis without recrystallization. Alcohols would been the only practicable solvents for this purpose, but some experi s made in this direction led us to fear the contaminating effects of ›lytic action. As we have pointed out above, the salts were probably or less contaminated with each other, and perhaps, also with the free . Under the circumstances, we have not thought it desirable to make ge number of determinations, in the hope that some of them might more closely with the results of theoretical computation. In of the wide divergence to be observed in many cases, we think that

the numerical results make plain the one point which we wish to emphasize at this time, namely, that the light colored salts contain about one molecule of acid more than the dark ones. The results follow:

Benzylidene p-Aminodimethylaniline.—Red hydrochloride: calculated for $C_{15}H_{16}N_2HCl$, Cl, 13.60; found, 17.01. Saturated hydrochloride: calculated for $C_{15}H_{16}N_2.2HCl$, Cl, 23.09; found, 20.48.

Cinnamylidene p-Aminodimethylaniline.—Red hydrochloride: calculated for $C_{17}H_{18}N_2HCl$, Cl, 12.36; found, 15.33. Saturated hydrochloride: Calculated for $C_{17}H_{18}N_2.2HCl$, Cl, 21.95; found, 21.34.

Piperonylidene p-Aminodimethylaniline.—Red hydrochloride: calculated for $C_{16}H_{16}O_2N_2HCl$, Cl, 11.63; found, 15.19. Saturated hydrochloride: calculated for $C_{16}H_{16}O_2N_2.2HCl$, Cl, 20.78; found, 21.12, 21.05.

Salicylidene p-Aminodimethylaniline.—Red hydrochloride: calculated for $C_{15}H_{16}ON_2HCl$, Cl, 12.81; found, 13.07. Saturated hydrochloride: calculated for $C_{15}H_{16}ON_2.2HCl$, Cl, 22.65; found, 22.47.

The color of the salts seemed less permanent in this case than in any we had previously studied. Nuth records that the free base turns red on standing in the air, and we notice that the red hydrochloride has a tendency to grow lighter in color. What is perhaps more curious is that the saturated hydrochloride which, when first precipitated, is almost colorless, grows considerably darker in color. We have since met with even more marked changes of this kind in the study of the bases formed by condensing *p*-aminodiethylaniline with aldehydes. We consider any theoretical discussion of this phenomenon to be premature until these diethyl compounds have been more thoroughly studied. The fact should be borne in mind, however, that, according to Anselmino, salicylic acid is one of those which forms isomeric aniles, one red, the other yellow.

Anisylidene p-Aminodimethylaniline.—Red hydrochloride: calculated for $C_{16}H_{18}ON_2HCl$, Cl, 12.20; found, 12.20. $C_{16}H_{18}ON_2.2HCl$, Cl, 21.68; found, 18.34. Saturated hydrochloride: calculated for $C_{16}H_{18}ON_2.3HCl$, Cl, 29.27; found, 28.78, 26.16, 26.61.

In view of the fact that in the case of the red hydrochlorides high results for chlorine are usually obtained, probably owing to the tendency of these salts to enclose some of the saturated compounds, the numerical results given above leave it a little in doubt whether the red salt, in this case, contains, when pure, one or two molecules of acid. It is quite evident, however, that the saturated salt contains nearly three molecules. This seems to be one of those cases referred to by Baeyer[1] where a base shows itself capable of combining with more acid than its formula accounts for. It might be supposed that in both salts the additional molecule of hydrochloric acid attached itself to the methoxyl group to

[1] Ber., 38, 1157 (1905).

form an oxonium salt. This may be the correct explanation, but it is not necessarily so; for we find that the most simply constituted member of the whole group, benzylidene aniline, though it conains but one nitrogen and no oxygen, yet adds two molecules of hydrochloric acid, as shown by the following analysis:

Calculated for $C_{13}H_{11}NHCl$, Cl, 16.29; for $C_{13}H_{11}N.2HCl$, Cl, 27.90; found, 27.68, 27.62.

We were much surprised at this result, as it raised the question whether all of the benzylidene compounds containing one nitrogen might not behave similarly, and whether in those containing two atoms, all of the acid might not be held by one nitrogen. The analyses of the salts of the three following compounds, however, show that the addition of more molecules of acid than there are nitrogen atoms in the base, is the exception; though from what has gone before, it may well be of more frequent occurrence than has hitherto been supposed.

Piperonylidene Aniline.—This base was first prepared by Lorenz.[1] It is absolutely colorless, the first of these compounds which we have been able to prepare in that condition. The hydrochloride is bright yellow, and this makes perhaps the most striking example of simple "halochromy" which we have observed in the group. The hydrochloride contains but one molecule of acid, as is shown by the following analytical data:

Calculated for $C_{14}H_{11}O_2NHCl$, Cl, 13.55; found, 13.76, 13.51.

Piperonylidene p-Toluidine.—This substance crystallizes from alcohol in cream-colored prisms which melt at 98°.

Calculated for $C_{15}H_{13}O_2N$, C, 75.26; H, 5.48; N, 5.87. Found, 75.28, 5.55, 6.11.

The hydrochloride is light yellow. The percentage of chlorine was determined. Calculated for $C_{15}H_{13}O_2NHCl$, Cl, 12.86; found, 13.03, 12.98.

Piperonylidene p-Chloraniline.—The base melts at 78°. It has not been analyzed. It forms a light yellow hydrochloride. Calculated for $C_{14}H_{10}O_2NCl.HCl$, Cl, 23.95; found, 23.43.

We wished to learn something of the color of salts analogous to those formed by condensing aldehydes with *p*-aminodimethylaniline, but which contained an amino group not substituted by alkyl radicles. We had some hopes that at least a small yield of such compounds might be obtained by condensing one molecule of aldehyde with one of a diamine. Accordingly we treated piperonal with *p*-phenylenediamine, and also with benzidine. In both cases the only products we obtained were those formed by the condensation of one molecule of diamine with two molecules of piperonal. These bases are soluble with difficulty in alco-

[1] Ber., 14, 792 (1881).

hol, ether, or the aromatic hydrocarbons. They can be crystallized from nitrobenzene, from which they separate in bronze yellow scales of a semi-metallic luster. The compound with *p*-phenylenediamine melts at 216°. Calculated for $C_{22}H_{16}O_4N_2$: C, 70.94; H, 4.33; N, 7.55. Found, 70.30, 4.52, 7.90.

The compound formed by condensing benzidine with piperonal melts not quite sharply at 241°. The liquid formed is not transparent, and it is possible that it is crystalline in character, as liquid crystals are not infrequently met with among compounds of similar constitution. The composition of the base was verified by a nitrogen determination. Calculated for $C_{28}H_{20}O_4N_2$, N. 6.50; found, 6.43.

We add some incomplete data concerning some substances prepared during the present investigation, but which, as they have no further theoretical interest for us, will probably not be worked with further.

Piperonylidene p-Aminoethylbenzoate.—This substance was prepared by condensing piperonal with *p*-aminoethylbenzoate. The base melts at 109°, is almost colorless, and forms a yellow hydrochloride.

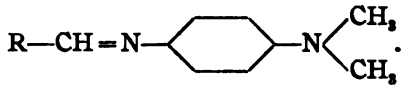
Calculated for $C_{17}H_{15}O_4N$, C, 68.64; H, 5.09; N, 4.72. Found, 68.34, 5.08, 4.84.

Piperonal condenses readily with *m*-nitraniline to form a base which melts at 119°. This forms a yellow hydrochloride. We have a nitrogen determination in the free base. Calculated for $C_{14}H_{11}O_4N_2$, N, 10.35; found, 10.56.

Piperonal condenses with *p*-bromaniline to form a product melting at 109°. This forms a hydrochloride of a light canary-yellow color. We have analyzed neither the base nor the salt.

Summary.

When *p*-aminodimethylaniline is treated with aromatic aldehydes, condensation products are formed which have the general formula



These bases add one molecule of hydrochloric acid to form dark red salts of a much deeper color than the free bases. The addition of more hydrochloric acid produces salts of a light yellow color, lighter than that of the free base.

Three explanations of this behavior are considered:

(1) That the first molecule of acid adds to the auxochrome nitrogen augmenting the color, while the second adds to the chromophore nitrogen, changing its valence and consequently destroying its chromophore character.

(2) That the monohydrochloride has a quinoid structure, while the saturated salt and the free base are benzoid.

(3) That there is a double series of stereoisomeric red and yellow base d salts, the red form of the monohydrochloride being the stable one, th llow form being stable in the other cases.

A decision as to which of these explanations is most applicable mus deferred until more experimental material can be collected.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
January 1, 1908.

ONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY

ON THE OXIDATION OF META-NITROBENZOYL CARBINOL.

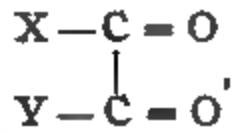
BY WILLIAM LLOYD EVANS AND BENJAMIN T. BROOKS.

Received January 15, 1908.

The work of Nef[1] on the oxidation phenomena exhibited by many seri organic compounds has made it possible to follow by experiment th act course taken by such reactions. The recent work of Denis[2] on th havior of various aldehydes, ketones and alcohols towards oxidizin ents is an excellent example of this kind of experimental study. In evious paper by one of us,[3] it was shown that reactions of this type i e benzoyl carbinol series lend themselves admirably to this kind of trea ent.

Zincke[4] and his students were the first to show that benzoyl carbin en acted upon by various oxidizing agents, gives mandelic, benzoy mic and benzoic acids in varying amounts according to the agents use a further study of this same substance by one of us,[5] it has been show at benzoyl-formaldehyde is also one of the products of oxidation of be yl-carbinol. When benzoyl- formaldehyde is acted upon by alkalies d copper salts,[7] at 100°, it undergoes a benzilic acid rearrangemen ing mandelic acid exclusively. It has been shown by Denis that acet maldehyde undergoes a similar rearrangement with dilute solutio sodium hydroxide, and even with water alone at 100° it suffers a pa l transformation.[8]

It is a well-known fact that many orthodicarbonyl compounds,

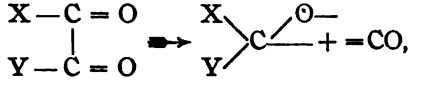


[1] Ann. Chem., 318, 137; 335, 191; 357, 214.
[2] Am. Chem. J., 38, 561.
[3] Evans, *Ibid.*, 35, 115.
[4] Ber., 13, 635; Ann. Chem., 216, 311.
[5] *Loc. cit.*
[6] Pechmann, Ber., 20, 2904; 22, 2556.
[7] Evans, Am. Chem. J., 35, 124.
[8] *Ibid.*, 38, 584, 585.

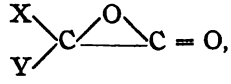
by the addition of one molecule of water, undergo a benzilic acid rearrangement, giving an α-hydroxy acid,

$$X.Y.C.(OH).COOH.$$

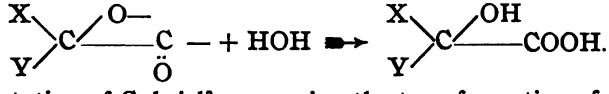
In some cases, such as diketosuccinic ester, hexaketomethylene and diketobutyric ester,[1] this transformation takes place in the presence of water, but in most instances the presence of an alkali is necessary. For this remarkable rearrangement Nef[2] has offered the following explanation: The orthodicarbonyl compound undergoes the following dissociation:



these products of dissociation then uniting to form an α-lactone,



which then, with a molecule of water, undergoes hydrolysis, forming the corresponding α-hydroxy acid, as:



The interpretation of Gabriel[3] concerning the transformation of *o*-carboxylbenzoyl-formaldehyde into phthalidcarbonic acid through the intermediate formation of *o*-carboxylmandelic acid becomes, therefore, perfectly evident. Upon this basis, also, the behavior of benzoyl formaldehyde, $C_6H_5=X$, $H=Y$,[4] towards oxidizing agents was readily explained. With mercuric oxide and silver oxide the reactions merely progress through the first stage, the rate of oxidation of the dissociated particles being greater than that of recombination. With copper hydroxide and potassium ferricyanide, in the presence of alkalies, the reaction progressed through the second stage, mandelic acid being the product in each case. The presence of benzoylformic acid in the oxidation with alkaline potassium permanganate is due to the subsequent oxidation of the mandelic acid formed in the second stage, as has been shown by precise experimental data.

Further experiments have been undertaken in this laboratory having for their main purpose: (1) to ascertain whether the same general course of reaction is followed in the substituted benzoyl carbinols as has been developed previously, and (2) to discover what possible effect, if any, the introduction of substituents into the ring might have on these substances towards the oxidizing agents previously considered. This paper, which constitutes a first report on this work, deals solely with the oxidation of

[1] Denis, Am. Chem. J., 38, 590.
[2] Ann. Chem., 335, 272, 273.
[3] Ber., 40, 81, 82.
[4] *Loc. cit.*

nitrobenzoylcarbinol. Briefly, the results are as follows: (1) *m*-Nitro ylcarbinol with freshly precipitated mercuric oxide, freshly precipit ver oxide, and potassium permanganate alone, or in the presenc ustic alkalies, gives *m*-nitrobenzoic acid and carbon dioxide exclusi) *m*-nitrobenzoylcarbinol, with cupric hydroxide and caustic alk ves only *m*-nitromandelic acid; (3) *m*-nitrobenzoylcarbinol, with p m ferricyanide and potassium hydroxide, gives both *m*-nitrobe id and *m*-nitromandelic acid. By comparison, it is seen that the d ces thus far developed lie in the behavior of *m*-nitrobenzoyl car wards potassium permanganate and alkalies, and potassium ferricya d alkalies. The general method previously employed for the prep n of benzoyl carbinol was found to be the most convenient for the p tion of *m*-nitrobenzoyl carbinol, *viz.*, the hydrolysis of the corresp g acetate which had, in turn, been prepared from the bromide.

Experimental Part.

Preparation of m-Nitromonobromacetophenone.—The following me the preparation of *m*-nitromonobromacetophenone was found t ch more satisfactory than methods previously described in the li re.[1] A solution of 24.2 grams (one molecule) of bromine in 40 c loroform was allowed to flow slowly into a warm solution of 25 g e molecule) of *m*-nitroacetophenone dissolved in 200 cc. of the vent, the operation being carried on in the sunlight. The first red the successively added portions of the bromine solution was immedi charged, the final color of the reaction mixture being yellow. tilling the chloroform, taking up the residue in ether and washing ute sodium carbonate solution, the dried ethereal solution gave a llow, crystalline residue, which was identical in every respect with monobromacetophenone described by Korten and Scholl.[2] This me ve a theoretical yield of 37 grams, which, when purified from a mi equal portions of ether and ligroin (60°–80°), gave a melting-poi °. The same general procedure may also be followed in the prepar *m*-nitrodibromacetophenone. Into a boiling solution of 5 grams lecule) of *m*-nitroacetophenone, in chloroform, were added slowly ms (two molecules) of bromine dissolved in 25 cc. of the same sol operation being carried on in the direct sunlight. The quickly d zed reaction mixture was then treated as above, giving finally a 9.8 grams of a yellow oil, which solidified on cooling to light y stals melting at 61°[3] (Engler found 59°). Applying the above ge thod to the preparation of dibromacetophenone, 20 grams (one mole monobromacetophenone, prepared according to the direction of Möh

[1] Hunnius, Ber., 10, 2008. Korten and Scholl: *Ibid.*, 34, 1909.
[2] *Loc. cit.*
[3] Ber., 18, 2240.
[4] *Ibid.*, 15, 2464.

were dissolved in 100 cc. of boiling chloroform and to this solution were added slowly 16 grams (one molecule) of bromine in 30 cc. of the same solvent. A final yield of 27.0 grams (theory = 27.9 grams) of the crude substance was thus obtained.

Preparation of m-Nitroacetophenone Acetate.—In preparing the ω-acetate of *m*-nitroacetophenone the same general method was followed as previously indicated by one of us in the preparation of the ω-acetate of acetophenone. It was found in the experiment herewith described that the temperature had to be carefully controlled owing to the tendency of the reacting substances to form tar. A mixture of 15 grams (one molecule) of *m*-nitrobromacetophenone, dissolved in 60 cc. of glacial acetic acid, and 7.56 grams (1.5 molecules) of powdered fused sodium acetate, was heated under a reverse condenser on an oil bath, the temperature being brought gradually to 105°, at which point it was maintained for two hours. Sodium bromide began to separate out at 90–95°, the larger portion coming down, however, at 105°. Finally the temperature was raised to 115° for one hour, after which the reaction mixture was poured into six volumes of water. The separated reddish-brown oil soon solidified on standing, after which the crystals were filtered and dissolved in ether. To this solution of the acetate was added that which was obtained by extracting the filtrate six times with ether. The combined solutions were washed with dilute sodium carbonate, after which the dried ether was evaporated to one-fifth of its volume, whereby the acetate began to crystallize out. By successive evaporation of the mother-liquor, a yield of 13.3 grams (theory = 13.7 grams) of the *m*-nitroacetophenone acetate was finally obtained. The substance (m. p. 51°), purified from a mixture of ether and ligroin, gave the following analysis:

Calculated for $C_{10}H_9O_5N$: C, 53.81; H, 4.03; N, 6.30. Found: C, 53.89, 53.80; H, 4.10, 4.10; N, 6.70.

Preparation of Meta-Nitrobenzoylcarbinol.—Twenty-five grams of *m*-nitroacetophenone acetate were hydrolyzed by means of 500 cc. of boiling water containing 1 cc. of dilute (1 : 1) sulphuric acid, the time of hydrolysis being thus reduced from nine to four hours without apparently increasing the yield of tar. After filtering and cooling, 16 grams (theory 20.5 grams) of the light yellow crystalline carbinol were obtained (m. p. 92.5–93°), this yield comprising the product also obtained by the evaporation of the second filtrate to one-fourth of its volume under diminished pressure. The aqueous solution of the carbinol reduces ammoniacal silver nitrate and Fehling's solutions. The analysis of the substance, purified from benzene, was as follows:

Calculated for $C_8H_7O_4N$: C, 53.03; H, 3.86; N, 7.73. Found: C, 53.20, 52.97; H, 3.88, 3.83; N, 8.50.

The following special experiment was performed: 0.20 gram of *m*-nitro-

benzoylcarbinol, dissolved in 1 cc. of glacial acetic acid, was act
0.5 cc. of acetyl chloride for one hour at 50°. The oil, obtained
ing the reaction mixture into 25 cc. of water, soon crystallized
0.18 gram of a product which when purified from ether-ligroin v
to be identical with the acetate above described.

m-Nitrobenzoyl Carbinol, Cupric Hydroxide and Sodium Hy
m-Nitrobenzoyl carbinol, like benzoyl carbinol and acetol, redu
ing's solution in the cold and also like these two latter substan
with alkaline cupric hydroxide the corresponding α-hydroxy
m-nitromandelic acid. The point of dissociation of the salts o
and secondary alcohols being much lower than the free alcol
reaction undoubtedly proceeds as follows:

$$NO_2.C_6H_4CO.CH_2ONa \rightarrow NO_2.C_6H_4.CO.CH\langle \quad +HON$$

the *m*-nitrobenzoylmethylene thus formed is then oxidized to
benzoylformaldehyde, which in turn, in the presence of the alka
goes a benzilic acid rearrangement to *m*-nitromandelic acid.[2] The
of behavior of *m*-nitrobenzoyl carbinol to acetol and benzoyl c
shown by the following experiment: To a solution of 2.0 grams (
cule) of *m*-nitrobenzoyl carbinol in 300 cc. of water were added
(two molecules) of crystalline copper sulphate in 20 cc. of w
the addition to the mixture of 3.31 grams (7.5 molecules) of so
droxide dissolved in 20 cc. of water, an instantaneous reduction t
oxide took place in the cold. After standing 24 hours the yel
was filtered and washed till the total volume was 800 cc.
with dilute sulphuric acid (1:1) and extracting 6 times with eth
of 1.93 grams of *m*-nitromandelic acid was obtained (theory 2.1
A study of the action of copper salts on *m*-nitrobenzoyl carbi
being made in this laboratory in the hope of obtaining the int
aldehyde. In preliminary experiments with cupric sulphate a
obtained which did not react with Fehling's solution even after
boiling and which, with phenylhydrazine, gave a beautiful yell
crystalline product.

m-Nitrobenzoyl Carbinol and Potassium Permanganate.—Th
difference in the behavior of benzoyl carbinol and *m*-nitrobenzo
towards potassium permanganate and alkalies is shown in the
experiment in which the substituted carbinol gave the corr
benzoic acid exclusively and no trace of the keto-acid as does
substituted substance. A mixture of 2.62 grams (three mol
potassium permanganate and 0.66 gram (three molecules)
hydroxide in 100 cc. of water was added to a solution of 1 gram

[1] Nef, Ann. Chem., 318, 138.
[2] Compare Evans, Am. Chem. J., 35, 125. Also Denis, *Ibid.*, 38, 584.

benzoyl carbinol in 150 cc. of water, the resulting temperature being 28°. The color of the first additions of the permanganate was instantly discharged, the reaction being accompanied by a gradual separation of the oxide of manganese. After standing four hours, the excess of permanganate was reduced with a few drops of alcohol, after which the aqueous filtrate was worked up in the usual manner. There was obtained 0.86 gram of the pure *m*-nitrobenzoic acid (theory = 0.92 gram). A solution of 5.22 grams of potassium permanganate in 100 cc. of water when added to a solution of 2 grams of *m*-nitrobenzoyl carbinol in 300 cc. of water, reacted instantly when carried out as in the previous experiment, a final yield of 1.78 grams (theory = 1.84 grams) of pure *m*-nitrobenzoic acid being obtained—a result in harmony with the studies on benzoyl carbinol. *r*-Lactic acid and *r*-mandelic acid are alike in their general behavior towards alkaline potassium permanganate in that both give acetylformic acid and benzoylformic acid, respectively.[1] In striking contrast to this general behavior is that of *m*-nitromandelic acid, which with these agents gives *m*-nitrobenzoic acid exclusively as is proved by the following experiment: A mixture of 2 grams of *m*-nitromandelic acid and 0.84 gram of potassium hydroxide in 50 cc. of water was added to a solution of 3.20 grams (two molecules) of potassium permanganate and 1.12 grams (two molecules) of potassium hydroxide in 100 cc. of water. After standing twenty-four hours, a yield of 1.61 grams (95 per cent. of theory) of pure *m*-nitrobenzoic acid was obtained. From this behavior of *m*-nitromandelic acid towards alkaline potassium permanganate, it was concluded that *m*-nitrobenzoylformic acid should also be completely oxidized to *m*-nitrobenzoic acid. That this expectation was fully realized is shown by the following experiment: To a solution of 4.03 grams (one molecule) of *m*-nitrobenzoylformic acid and 1.03 grams (1.25 molecules) of sodium hydroxide in 100 cc. of water was added a solution of 3.45 grams of potassium permanganate in 100 cc. of water. After standing at room temperature for twenty-four hours the reaction mixture yielded 3.29 grams (theory = 3.45 grams) of *m*-nitrobenzoic acid.

m-Nitrobenzoyl Carbinol, Potassium Ferricyanide and Potassium Hydroxide.—*m*-Nitrobenzoyl carbinol in its behavior towards alkaline potassium ferricyanide is different from benzoyl carbinol in that it gives *m*-nitrobenzoic acid in addition to its corresponding hydroxy acid, as the following experiment shows: One gram of *m*-nitrobenzoyl carbinol dissolved in 150 cc. of water was added to a mixture of 10.91 grams (six molecules) of potassium ferricyanide and 2.48 grams (eight molecules) of potassium hydroxide dissolved in 100 cc. of water, the resulting temperature being 28.5°. After standing over night the solution was acidified with dilute

[1] Compare Ulzer and Seidel, Monatsh. Chem., 18, 138. Also Denis, Am. Chem. J., 38, 575.

.lphuric acid and extracted six times with ether. There was thus ob
ined 0.93 gram of acid material (m. p. 85–95°) which, upon dissolvin
15 cc. of hot water and cooling suddenly, gave 0.27 gram of a flak
ecipitate (m. p. 138–139°) which proved to be *m*-nitrobenzoic acid, th
ueous filtrate containing *m*-nitromandelic acid. A study of the be
vior of *m*-nitromandelic acid towards alkaline potassium ferricyanid
as made as follows: To a solution of 2.0 grams (one molecule) of *m*-nitr
andelic acid and 3.98 grams of potassium hydroxide (seven molecules
50 cc. of water were added 16.71 grams of potassium ferricyanide, th
sulting temperature being 24°. After standing twenty-four hours an
orking up as above a yield of 1.75 grams (m. p. 85–90°) of acid materi
as obtained which gave no reaction with phenylhydrazine[1] thus showin
e absence of *m*-nitrobenzoylformic acid. In view of this result, th
llowing experiment needs no further explanation: To a solution of 1.3
ams (one molecule) of *m*-nitrobenzoylformic acid and 1.00 gram
dium hydroxide, in 100 cc. of water, were added 13.47 grams of pota
um ferricyanide and 2.26 grams of potassium hydroxide in 100 cc.
ater. After standing at room temperature for 24 hours, the reactio
ixture yielded 1.10 grams (theory = 1.14 grams) of *m*-nitrobenzoic aci
he reaction mixtures when acidified with dilute sulphuric acid gave th
russian blue test with ferric chloride.

m-Nitrobenzoyl Carbinol and Silver Oxide.—*m*-Nitrobenzoyl carbin
hen acted upon by silver oxide either in the presence or absence
kalies gives *m*-nitrobenzoic acid, a result which is in harmony with th
tion of the same reagents on benzoylcarbinol and with the experimen
Denis on acetol.[2] It is perfectly evident that *m*-nitrobenzoyl carbin
ssesses a possibility of dissociating in two directions, viz.:

$$(1)\ NO_2.C_6H_4.CO.CH_2OH \rightarrow NO_2C_6H_4.CO.CH\langle \quad +HOH$$

$$\text{and}\quad (2)\ NO_2.C_6H_4.CO.CH_2OH \rightarrow NO_2.C_6H_4.CHO + H_2CO.$$

Consequently, in the absence of alkalies, it is possible for *m*-nitr
nzoic acid to arise from an oxidation of the dissociated particles i
uation (2).[3] One gram (one molecule) of *m*-nitrobenzoyl carbin
ssolved in 150 cc. of water was added to 2.5 molecules of freshly pr
pitated and well washed silver oxide, prepared from 4.68 grams of silv
trate. On standing nine hours at room temperature a slight reductio
as observed, accompanied by a brown coloration of the carbinol solutio
he temperature was raised to 70° for one hour and finally to 100° till th
olution of carbon dioxide ceased, determined by its action on bariu

[1] Fehrlin, Ber., 23, 1576.

[2] Am. Chem. J., 38, 579.

[3] Compare Evans, Am. Chem. J., 35, 129. Nef, Ann. Chem., 335, 269. Al
ling, Ann. chim. phys. (8), 5, 529.

hydroxide solution. Treating the reaction mixture with an excess of ammonium hydroxide, carefully acidifying the filtrate from the metallic silver and working up in the usual way, there was obtained 0.80 gram (theory = 0.92) of *m*-nitrobenzoic acid. The action of *m*-nitrobenzoyl carbinol on silver oxide in the presence of alkalies was carried on as follows: A solution of 1 gram of the carbinol in 150 cc. of water was added slowly to four molecules of freshly precipitated and well washed silver oxide (from 4.68 grams of silver nitrate) suspended in 50 cc. of an aqueous solution of sodium hydroxide containing 1.13 grams, the resulting temperature being 29°. At the end of three days the reaction mixture gave 0.74 gram (80 per cent.) of *m*-nitrobenzoic acid and 2.19 grams (theory = 2.56 grams) of metallic silver. The following special experiment shows that the presence of *m*-nitrobenzoic acid could not be attributed to the intermediate formation of *m*-nitromandelic acid and its subsequent oxidation. Two grams of *m*-nitromandelic acid and 0.85 gram sodium hydroxide dissolved in 100 cc. of water were added to an emulsion of 4.71 grams of freshly precipitated and well washed silver oxide, prepared from 6.94 grams of silver nitrate. After standing at room temperature for 24 hours and working up the reaction mixture in the usual way, 1.90 grams of the original acid were recovered. A similar result was obtained by allowing the reaction mixture to stand six weeks.

m-Nitrobenzoyl Carbinol and Mercuric Oxide.—The recent experiments of Denis[1] confirm the observations of Nef and Kling; namely, that acetol with mercuric oxide in the presence of alkalies gives *r*-lactic acid instead of acetic acid, as one would expect from the course of the analogous reaction in the aromatic series. *m*-Nitrobenzoyl carbinol is analogous to the behavior of benzoyl carbinol towards alkaline mercuric oxide as the following experiments show: A solution of 1 gram of *m*-nitrobenzoyl carbinol in 150 cc. of water was added to 2.5 molecules of freshly precipitated and well washed mercuric oxide (from 3.74 grams of mercuric chloride) and 1.54 grams of sodium hydroxide, reduction taking place instantly. After standing 24 hours the reaction mixture yielded 0.68 gram of *m*-nitrobenzoic acid. Repeating the same experiment but in the absence of alkali, there was obtained 0.84 gram of *m*-nitrobenzoic acid. In the latter experiment, however, the reaction mixture after standing 24 hours was kept on a boiling water bath for six hours, during which time a large amount of barium carbonate was precipitated from the attached barium hydroxide solution. A special experiment with *m*-nitromandelic acid and alkaline mercuric oxide showed that this substance is similar in its behavior towards these agents as it is towards silver oxide and caustic alkalies. One gram (one molecule) of *m*-nitromandelic acid and 1.10 grams of sodium hydroxide dissolved in 100 cc. of water, when

[1] *Loc. cit.*

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[1] J.

understood and repeatedly stated during the last three years in what may be called the commercial literature, that its chief constituent is terpineol. In the scientific literature however, I can find only one single reference to its composition. Walker,[1] from its distillation and from its formation of a hydrochloride melting at about 50°, surmised that it might contain a terpineol. His experiments, however, were made on a small amount of material produced on a laboratory scale only.

The commercial long leaf oil, as it comes on the market, is either clear and water white, containing 3 or 4 per cent. of dissolved water, or it may have a very faint yellow color and be free from dissolved water. The specific gravity ranges from 0.935 to 0.947, depending on freedom from lower boiling terpenes. A good commercial product will begin distilling at about 206° to 210° and 75 per cent. of it will distil between the limits 211°–218°, and 50 per cent. of it between 213–217°. A sample having a density of 0.945 at 15.5° showed a specific rotation of about $[\alpha]_D^{20°}$ —11°, and an index of refraction of N_D 1.4830. In fractional distillation of the oil the specific gravity of the various distillates rises regularly with increasing temperature, becoming steady at about 0.947 at 217°.

If the oil consists essentially of terpineol, $C_{10}H_{18}O$, it should be easy to convert it into terpin hydrate, $C_{10}H_{20}O_2 + H_2O$, by the method of Tiemann, and Schmidt.[2] The conversion was found to proceed easily when the oil was treated with 5 per cent. sulphuric acid, either with or without admixture with benzene. If agitated continuously, the reaction is complete within 3 or 4 days. If, on the other hand, the mixture is allowed to stand quietly, the formation of terpin hydrate extends over several months and produces most beautiful large crystals, which, without recrystallizing, melt at 117–118°. When recrystallized from ethyl acetate they melt at 118°. Yield, about 60 per cent. of the theoretical. This forms such a simple, cheap and convenient method of making terpin hydrate that it will doubtless supersede the usual manufacture from turpentine, alcohol and nitric acid, and instead of terpin hydrate serving as raw material for the manufacture of terpineol, as heretofore, the reverse will be the case.

Terpineol Nitrosochloride. — This compound was made in the usual manner from amyl nitrite, glacial acetic acid and hydrochloric acid. The yield was good and the product, after crystallization from ethyl acetate, proved to be very stable. Melting point 101–103°.

Terpineol Nitropiperidide.—This compound was made from the nitrosochloride and piperidine according to Wallach's method. The once recrystallized product melted at 158–159° and formed well-shaped crystals from methyl alcohol.

[1] Massachusetts Institute of Technology Bulletin, September, 1905.

[2] Ber., 28, 1781.

Terpineol nitranilide was made from the nitrosochloride and anili dissolved in alcohol. On dilution of the reaction mixture with a lit water good crystals of the nitranilide were obtained.

Dehydration Products.—Wallach[1] found that when 25 grams of t pineol were heated with dilute sulphuric acid, there resulted 16 cc. t pinene and cineol boiling at 177–180°, 4 cc. boiling at 181–185°, and cc. boiling at 185–187°, containing terpinolene. This experiment w repeated, using a sample of long leaf pine oil, of which nearly the wh distilled at 216–218°. 100 grams of this oil heated for one hour wi 400 cc. of dilute sulphuric acid (1:2) and then distilled with steam a dried over sodium, gave 85 cc. of oils volatile with steam. On redistil tion the following fractions were obtained: 5 cc. at 165–175°, 56 at 175–180°, 6 cc. at 181–185°, and 15 cc. at 186–192°. The larg fraction had a specific gravity of 0.860 and evidently consisted essentia of terpinene. It will be seen that these results agree quite closely wi those obtained by Wallach from pure terpineol.

In conclusion, the specific gravity, index of refraction and boiling poi of the long leaf pine oil, its absorption of bromine in quantity correspon ing to a dibromide, the formation of a nitrosochloride, nitropiperidi and nitranilide, the formation of terpinene by dehydration and the ea conversion and large yield of terpin hydrate leave little doubt that the sential constituent of long leaf pine oil is a terpineol and is probab the optically active levo modification of α-terpineol (Δ^1-*p*-menthenol(boiling at 217–218°.

This seems to be the first recorded occurrence of terpineol in any me ber of the pine family. Even in this case it was obtained not from t living tree but from lightwood, *i. e.*, from portions of the tree which h been cut at least three years and were very resinous. It is the comm belief of those familiar with lightwood that its resinous content increa regularly from the time it is cut from the tree or from the death of the tr If any such action occurs the appearance of terpineol here would se quite natural, as its formation from pinene requires only the additi of one molecule of water accompanied by splitting the tetra ring of pine

The investigation of this oil is being continued.

164 FRONT ST., NEW YORK CITY,
December, 1907.

TRANSPARENT SOAP—A SUPERCOOLED SOLUTION.

BY W. D. RICHARDSON.

Received January 15, 1908.

The alkali-metal salts of the fatty acids—commonly called soaps have been usually considered crystalloids by the older authorities and others in recent years as colloids.[2]

[1] Wallach, Ann., 230, 225.

[2] Leimdorfer, Seifensied. Ztg. 1906, Nos. 24-29; Merklen, Chem. Abs. 1907, 24 Lewkowitsch, J. Soc. Chem. Ind., 26, 590 (1907).

The criteria of colloids are: (1) slow or no diffusion through colloidal membranes; (2) failure to raise the boiling-point or lower the freezing-point of solvents; (3) electrical migration; (4) coagulation phenomena; (5) absorption phenomena; (6) hysteresis; (7) impenetrability for other colloids; (8) optical inhomogeneity; (9) separation by salts ("salting out"). Of these criteria at least (2), (5), (7), and (9) hold good for soap.

It is probably true that many facts in regard to the formation of soap and also many properties of finished soaps can be explained on the assumption that they are colloids forming in solution reversible hydrosols in the classification of Zsigmondy,[1] but it is equally true that they crystallize, if not quickly, at least slowly and definitely. In all likelihood the ordinary pure soap of commerce consists chiefly of a compact mass of soap crystals embedded in a non-crystalline soap phase. A thin section of such a soap transmits light through crossed Nicols and while this phenomenon can be explained upon other assumptions, the facts of opacity and the presence of straight line boundaries indicate the presence of masses of crystals. Possibly the best view to take of the matter would be to consider soap as a substance with distinctly crystalline tendencies, which on account of the size of its molecules, its viscosity and its solubility, which varies considerably with the temperature, exhibits colloidal properties.

In cold water many of the alkali metal salts of the saturated higher fatty acids are but sparingly soluble, whereas at temperatures under 100° and ordinary pressures, solutions are readily formed consisting of 70 to 80 per cent. of soap and 30 to 20 per cent. of water. These solutions are quite transparent, but upon cooling they become opaque. The opacity of some soaps is in part due to the presence of an emulsion of soap and fatty matter, and this is well illustrated in the case of cold-made soaps, in which saponification is purposely left incomplete; but in the instance mentioned the opaque mass is formed of pure soap and water.

A soap may, however, be of such a composition that when it solidifies, instead of becoming opaque, it remains clear and such a soap is known in the trade as transparent soap. A familiar example of such a product is a cooled alcoholic solution of soap. This, upon solidification, assumes the appearance of a jelly and if not perfectly transparent is at least translucent. A solidified dilute water solution of soap is also frequently translucent; but whether the jelly be made with alcohol or water, soap crystals of rather imperfect shape usually form in time. It may be said in passing that transparency in soap is not a mark of purity or even of definite composition. Probably a better soap can be made of the ordinary opaque sort. The best known brand of transparent soap on the market contains 20 per cent. of rosin, calculated on the basis of total

[1] Zsigmondy, Zur Erkenntnis der Kolloide.

acids, and rosin must be considered as an inferior soap-making materia
The demand for a transparent soap must be attributed to a whim
that portion of the public to whom transparency is synonymous wi
purity.

In commercial transparent soaps there are usually present one or mo
substances which appear to act as retarders, preventing crystallizatio
Among these substances are glycerol, ethyl and methyl alcohols, ca
sugar and alkali-metal salts of rosin. Also certain soaps (such as t
sodium soap of castor oil) seem to have this power. While some of the
substances, at least under certain conditions, maintain th
parent state by means of a considerable solvent powe
they appear to act simply as retarders, preventing or h
lization. In mentioning retarders, the action of certain
as protein substances boiled with lime water, upon the se
Paris might be cited. One part of retarder to one tho
may retard the setting time an hour or two; large quan
it an infinitely long time. Such seems to be the action of
stances mentioned upon the crystallization of soaps.
another way also (since some are hygroscopic) by preven
desiccation under ordinary circumstances and, therefor
the soap from assuming the supersaturated condition. Thus some tran
parent soaps which would never form crystals when exposed to the a
do so when kept in a desiccator over calcium chloride or sulphuric ac
When removed from the desiccator and placed in a moist chamber t
soap swells, absorbs water and the crystals in time dissolve. The sa
soap, returned to the desiccator, may not form crystals the second tim

It is ordinarily stated in text-books that there are two ways of prepa
ing transparent soap; one by dissolving dry soap in alcohol, distilling
the alcohol and moulding the syrupy residue; the other by "filling
molten soap with sugar, syrup, etc. As a matter of fact, there are n
two but many ways of manufacturing transparent soap, but the pri
ciple in all cases is essentially the same, namely adding to a soap sol
tion substances which will form a jelly and retard crystallization. Pu
soap, when dissolved in alcohol and the alcohol distilled off entire
or in part, will form not a transparent soap, but an opaque one. If t
20 per cent. of rosin were left out of the brand for which the first proce
mentioned above is claimed and if no glycerol were present, it is que
tionable whether or not a transparent soap would be the result. O
formula for transparent soap commonly given in the literature is:

Tallow	100 parts
Cocoanut oil	100 "
38° Bé. caustic soda solution	150 "
Glycerol	40 "
Alcohol	80 "

Explanation of Plate.

A, B and C, cakes of transparent soap containing naturally occurring soap crystals; A and B contain many disc-shaped crystals, C fewer. D, E, F and H contain crystals which have been formed by seeding molten soap with crystal fragments from A and B. In the lower part of D is an area where crystals have not formed, probably owing to absence of nuclei. G is a bar in which a rod of soap containing crystals, cut from C by means of a cork borer, has been inserted and from which crystals have grown, although they do not show well in the illustration.

This formula does not make a transparent soap but a decidedly opaque and crystalline one. One hundred parts of castor oil and the necessary caustic soda may be added besides, the glycerol and alcohol may be trebled, but the product is still opaque. If now rosin soap is added or cane sugar, or both, a perfectly transparent soap results.

As transparent soap comes from the kettle it is quite clear and transparent; after solidification in frame or mould it is usually, though not always, less clear. After partial desiccation it becomes quite transparent again to the eye, when viewed with ordinary light, although it probably diffuses light to some extent. Immediately after manufacture transparent soap does not transmit light between crossed Nicols but with age this property increases until finally, when viewed even in thin sections, a soft bluish light is transmitted by such soaps of the most varied compositions. It is the usual rule with transparent soap that after aging it reaches a condition after which no great change ensues; the bars remain transparent and firm and do not lighten or darken in color. But occasionally soap crystals form in a bar which is in all visible respects like the normal bar; further, these crystals may form in a bar of identical composition with one free of crystals; the bar with crystals and the one without may indeed have come from the same batch of soap or the same frame. The crystals when first visible are about one-half millimeter in diameter; they may enlarge until a diameter of fifteen millimeters is reached. When one millimeter in diameter they appear under the microscope in section as fine needles radiating from a center, which is somewhat opaque, into a clear matrix. Between crossed Nicols the appearance is striking. The central portion transmits light in a marked manner and appears red and yellow; surrounding the central portion in a circle of bluish light; surrounding this and reaching almost to the crystal-needle ends is a black ring. Just outside the crystals is a bright bluish ring; this is in the transparent region and beyond this is the uniform dim bluish area characteristic of the non-crystalline soap. The outer bright, bluish ring would appear to indicate a condition of unusual strain in the soap. The crystals usually become noticeable in from four to eight weeks and they grow in size and numbers for an indefinite time, depending on conditions. Sometimes they appear in as short a time as one week and again they may not become visible for from eight to ten months. In some cases only a few crystals develop, in others the bar finally appears as a mass of soap crystals lying in a clear matrix. Attempts have been made to separate the crystals from the matrix by solution in hot and cold alcohol and water and other solvents, but unsuccessfully, although the crystals differ to some extent in their physical behavior from that of the transparent portion of the soaps. The crystals have been separated by hand in small quantities by excision, and

their analysis indicates their composition to be that of ordinary p soap. The amount of material thus separated was small and proba impure, owing to the fine needle form of the crystals and their ramify tendency. The fatty acids were separated from them as well as f the clear matrix surrounding them and melting-point determinati made upon the acids. Those from the crystals melted at 43–44°, w those from the clear portion melted at 36–38° C. These figures est lish little beyond the fact that it is the soaps of the harder fatty a which form the crystals and that these soaps are probably compo of saturated acids, for the melting-points of unsaturated fatty acids low.

The facts indicated above, that crystals form in one bar of soap not in another when both are from the same batch and that the in duction of soap crystals leads to the formation of crystals in other non-crystalline bars, would lead to the conclusion that nuclei of s sort are one of the essentials leading to crystal formations. There another fact of interest in this connection, namely that crystals are quently formed abundantly in the interior of a bar whereas the surf to a depth of from two to six millimeters is free from crystals. It is parent that this condition is connected with the progress of desicca in the cake, for the line of demarcation between well dried surface moister interior corresponds closely with the boundary between c talline and non-crystalline soap. The surface of soap dries quickly a depth of about one millimeter, but thereafter the desiccation is tremely slow, inasmuch as the surface skin so formed protects the inte against the loss of moisture. The dried portion is very hard and to and consequently possessed of great viscosity and rigidity. In suc medium, even though it be supercooled, crystal formation is almost not quite, impossible.

I have used the term "supercooled" in referring to transparent soaps ra than "supersaturated," because the substance is in the solid conditio amorphous and may start to crystallize at once upon solidification f the kettle without any evaporation of the solvent. While there be a slight impropriety in the use of the term, it appeared fully as us in describing the properties of the soap as the term "supersaturated."

Now the characteristic of the supercooled or supersaturated co tion is its instability as regards crystallization. The means suffic for bringing about equilibrium are shock, or the introduction of a or isomorphous crystal. Viscosity or rigidity in an amorphous substa may render crystallization extremely slow or prevent it altogether. example, the devitrification of glass is usually a very slow process.

If a soap crystal be introduced into a bar of transparent soap an the solvents are not present in excess (that is, if the soap is indeed in

dition for crystallization) radiating crystals will start to grow from the one introduced and will spread to an indefinite extent through the soap, if sufficient time be allowed. If soap crystals be ground in a mortar and ever so small a weight of them be introduced into transparent soap as it is about to solidify, the soap will in time become a mass of crystals. If, on the other hand, the same weight of soap crystals be dissolved in a small quantity of alcohol, and this solution added to the molten transparent soap, and if the soap be then filtered as a special precaution against the introduction of nuclei, no crystals will form. In one series of experiments holes were made by means of a cork borer in bars of transparent soap, which contained no crystals, and into these holes, plugs of soap cut from a crystalline bar with the same cork borer were pressed. Around the plugs so introduced masses of crystals formed and are still forming, although some of the experiments are now a year and a half old. In the parts of the bars remote from the crystalline plug no crystals have formed at all. Not all nuclei induce the formation of crystals. For instance, in one series of experiments particles of crystalline silica were incorporated in molten soap, and these, during one and one-half years' time, developed no crystals, although soap of identical composition, when seeded with soap crystals, produced a large crop. Experiments on various substances as nuclei are now in progress.

The influence of shock or physical strain in the production of soap crystals is shown by the tendency of the crystallization to proceed in certain planes which follow the lines of strain produced in the soap by the impress of the die used in stamping the bars. This produces crystals, in the form of circular discs (of radiating needles) rather than spheres; also the crystals near the surface frequently cluster around a line or edge where the die has struck, rather than against a plane surface of the soap.

It will be seen that no one explanation will account for the formation of crystals in transparent soap under all conditions. The inertia or hysteresis attending change of state may be accentuated or retarded in this case as in others by a variety of circumstances. The principal influences and conditions affecting the formation of crystals may be grouped as follows:

(1) Supersaturation or the supercooled condition presupposing a condition of strain.

(2) Absence of sufficient quantities of retarders to prevent crystallization altogether.

(3) Desiccation: provided the soap is not supersaturated at the time of manufacture, desiccation is necessary to bring about conditions suitable for crystal formation. As desiccation proceeds there is apparently an increase in strain produced in the soap as shown by the transmission of light between crossed Nicols.

(4) Nuclei appear to be the principal exciting cause of crystal for
on when other conditions are favorable. These nuclei are soap c
als or particles and possibly other substances. Experiments are
progress in regard to this point.

(5) Not too great viscosity or this may overcome the crystalli
orces. Rapid desiccation may entirely prevent crystal formation.

(6) Shock produced by blows or pressure act favorably on cry
ormation in many cases.

In conclusion, crystal formation, while it does not reduce in any
ree the detergent power of a soap, renders it more or less unsalabl
public which buys according to the appearance of goods. The exp
ental work detailed above was undertaken in order to examine
ematically the causes of crystal formation in transparent soap an
rovide a remedy.

CHEMICAL LABORATORIES OF SWIFT & CO.,
CHICAGO.

NOTES.

Rapid Determination of Petroleum Naphtha in Turpentine.—To
ermine the amount of petroleum naphtha in a suspected sampl
urpentine, 10 cc. are carefully measured into a 50 cc. carbon tube, w
graduated into tenths of a cubic centimeter.

Thirty cubic centimeters of aniline are now added and the mixture
ntly shaken for five minutes, and left to settle until the liquid has
ome perfectly clear, when, if there is any petroleum naphtha pre
the turpentine, it will be thrown out of solution and float in a
n top, and the percentage can be readily ascertained. I get exce
esults from this method, but care must be exercised that the an
oes not contain any water. HENRY C. FRE

2821 REYNOLDS ST.,
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Determination of Sodium and Potassium in Silicates.—We
ound the following method of determining sodium and potassium in
nd silicates which can be decomposed by sulphuric and hydrofl
cids, rapid and satisfactory.

One gram of clay is decomposed by means of sulphuric and hy
uoric acids, and the excess of sulphuric acid expelled in a hot air
he residue is then dissolved in water and powdered barium hyd
le added to the boiling liquid to alkaline reaction. The solutio
ecanted and filtered and the residue boiled again with water and
ughly washed. Carbon dioxide is passed into the filtrate in ex
e solution evaporated to 50 cc., 25 cc. of alcohol (96 per cent.) ad

and the solution filtered and the residue washed with 50 per cent. alcohol. A measured excess of $N/10$ hydrochloric acid is then added to the filtrate and the solution boiled to expel the carbon dioxide, litmus being used as an indicator and more acid being added if necessary, to give a permanent acid reaction after boiling. The titration is then finished with $N/10$ sodium hydroxide. The solution is evaporated to dryness in platinum, dried at 110° and finally at very faint redness and the residue of potassium and sodium chlorides weighed. The amount of each metal can be calculated on the following principle:

Let a = No. of cc. of $N/10$ HCl used less the No. of cc. of $N/10$ NaOH.

$b = a \times A\ 0.00585$ = weight of NaCl equivalent to sum of NaCl + KCl.

c = weight of NaCl + KCl formed less the weight of NaCl corresponding to the weight of NaOH used.

x = weight of Na.

y = weight of K.

Then $b = \frac{58.5}{23.05} X + \frac{58.5}{39.15} y.$

$c = \frac{58.5}{23.05} X + \frac{74.6}{39.15} y.$

$y = 2.432\ (c-b).$

$x = \frac{23.05}{58.5}\left(c - \frac{74.6}{39.15} y\right) = 0.3937\ c - 0.75\ y.$

Three samples of clay gave by the above method:

	By Lawrence Smith's method.		By the above method.	
	K.	Na.	K.	Na.
A.....	0.76	0.14	0.77	0.14
B.....	0.33	0.53	0.33	0.45
C.....	0.18	1.39	0 14	1 42

J. E. THOMSEN.

LABORATORY OF JOSEPH DIXON CRUCIBLE CO.,
JERSEY CITY, N. J.

The Determination of Total Nitrogen Including Nitrates in the Presence of Chlorides.—Asboth, Jodlbauer and Scovell have modified the Kjeldahl nitrogen method with the view of making possible the determination of nitric nitrogen simultaneously with organic nitrogen. In the presence of common salt, however, these modifications, and also the method of the Official Agricultural Chemists (which is essentially Scovell's) are inapplicable; for the sulphuric acid used in the method acts upon chlorides and nitrates producing hydrochloric and nitric acids and before the latter is reduced to ammonia by the reducing agents present, the following reaction occurs:

$$HNO_3 + 3HCl \rightarrow 2H_2O + Cl_2 + NOCl.$$

The pickling solutions used for curing meats contain usually sal saltpeter and sugar; and after use they contain also the class of substanc known as meat bases and various proteins. Cured meats themselv also contain all these compounds. The Kjeldahl method and its mo fications are inapplicable, therefore, to the determination of total n trogen in cured meats and pickling solutions. Various methods we tried in this laboratory to arrive at the amount of total nitrogen in the two products and the following was devised for the purpose: (1) d termine nitric nitrogen by the Schloessing-Wagner method; (2) in a other portion determine nitrogen excluding nitrates by adding to t substance in the Kjeldahl flask 10 cc. more or less of saturated ferro chloride solution and boiling with dilute sulphuric acid until nitrat are destroyed. Then proceed with the determination of the remaini nitrogen by the Kjeldahl or Kjeldahl-Gunning method. The sum (1) and (2) gives the total nitrogen. A test solution was made contai ing ten grams ammonium chloride, ten grams potassium nitrate and 2 grams sodium chloride in 1000 cc. By the Kjeldahl method mo fied to include nitrates the following quantities of total nitrogen we found in three determinations in aliquot parts of this solution: 0.09 g., 0.0883 g. and 0.0834 g. calculated: 0.1000 g. By the method d scribed above the following quantities were found: nitric nitrogen 0.03 g. (calculated 0.0346 g.); other nitrogen by Kjeldahl method after r moval of nitrates, 0.0653 g. (calculated 0.0654 g.); total nitrogen fou 0.1000 g. (calculated 0.1000 g.). Mr. E. F. Scherubel assisted in th work.

W. D. RICHARDSON.

LABORATORY OF SWIFT & CO.,
CHICAGO.

REVIEWS.

REVIEW OF ANALYTICAL WORK DONE IN 1906.

BY BENTON DALES.

Received December 15, 1907.

In this review the only change from the plan of previous ones is th American work has been included. The writer's acknowledgment his indebtedness to the *Chemisches Zentralblatt* for general grouping subjects and for abstracts is due again and is here made. He has ma use occasionally also of abstracts in the *Journals of the London Che ical Society* and *Society of Chemical Industry*.

General Analysis.

Apparatus.—A new Orsat apparatus was proposed by Bendema (*J. Gasbel.*, **49**, 583, from *Z. Ver. Ing.*) for analysis of the new power ga which contain something like 30% of carbon monoxide, 12% of hydrog and only traces of methane. Two cuprous chloride pipettes are us and where considerable amounts of oxygen are to be absorbed eit

phosphorus or a second pyrogallol pipette. About 30 cc. of gas are taken for the combustion. The combustion pipette is best covered with a water jacket connected with the water mantle of the burette. Lux (*Ibid.*, **49**, 475) described the Raupp gas calorimeter as better than the Junker. It consists chiefly of a copper cylinder whose lower part is solid, the hollow upper part carrying a thermometer divided into tenths. Under the copper body is placed at a certain time the gas flame, whose height has been previously determined, and the time necessary for the thermometer to rise 10° is noted. The apparatus is standardized by means of gases of known heating value, so from a table and from the measured time the heating value can be calculated. McDowall (*Chem. News*, **94**, 104) recommended the use, instead of the ivory scale on balances, of a brass one which should move by a horizontal screw under the box engaging a tooth attached to the scale. After the pans are released the scale may be moved till the pointer swings equally on either side of the zero. An apparatus was described by Weimern (*J. russ. phys.-chem. Ges.* **38**, 228) for determining the solubility of solids in liquids. It consists essentially of two glass cylinders held together by an oblique tubular connection projecting downward inside the lower cylinder. The liquid is saturated with the solid in the upper cylinder which has a large stirrer that is used also to force the liquid through the side arm containing a wadding tampon and so into the weighed glass receiving vessel. The lower cylinder has an arrangement by which the cover of the weighing vessel may be placed before the vessel is removed from the cylinder. It is then weighed, the liquid evaporated, and weighed again.

Combustion and Heating Value.—A good deal of work was published on the various combustion methods noted in previous reviews. Carrasco and Plancher (*Gazz. chim. ital.*, **36** II, 492) gave more details concerning their method of internal electrical heating in the use of which priority was claimed by Morse and Gray (*Am. Chem. J.*, **35**, 451). Dennstedt (*Z. angew. Chem.*, **19**, 517; *Z. anal. Chem.*, **45**, 26) and Dennstedt and Hassler (*J. Gasbel*, **49**, 45) gave more details with regard to Dennstedt's simplified combustion method. The second of these three articles is in reply to the criticisms of Hermann which were maintained by the latter (*Z. anal. Chem.*, **45**, 236). The last of the three contains the modifications of the method necessary for the analysis of coals. Holde (*Ber.*, **39**, 1615) and Holde and Schlüter (*Mitth. kgl. Materialprüfungsamt Gross Lichterfelde West*, **24**, 268) gave the results of some experiments with the Dennstedt and Heraeus furnaces, mentioning as some of the difficulties of Dennstedt's rapid method those of obtaining the correct agreement between oxygen addition and rapidity of combustion, the occasional failure of the platinum quartz to glow as a criterion for the proper carrying out of the method and the necessity of constant watching. Dennstedt (*Ber.*, **39**, 1623) replied, saying that the commonest error in the rapid method is the too rapid volatilization of the substance. This should be run with an oxygen current of about 60 cc. per minute instead of running the oxygen current according to the rapidity of volatilization. Von Konek (*Ibid.*, **39**, 2263) added his favorable experiences with the Heraeus furnace. Marek (*J. pr. Chem.* [2] **73**, 359; **74**, 237) recommended the use of a 5 cm. layer of copper oxide or copper oxide asbestos in combustion analyses instead of the layer of ordinary length. This proposal was criticized by Dennstedt (*Ibid.*, [2] **73**, 570).

A number of methods for determining the halogens in organic compound
:e proposed. That of Berry (*Chem. News*, **94**, 188) is a combinatio
those of Piria and Schiff (ignition with sodium carbonate and lime
l the thiocyanate method of Volhard. The cooled mass is dissolve
dilute nitric acid (1:4), kept cool, excess of tenth-normal silver n
te added, the silver halide filtered and the filtrate titrated with tenth
mal potassium thiocyanate, using ammonium iron alum as ind
or. With substances containing iodine, sodium carbonate alone
d for the ignition. Moir (*Proc. Chem. Soc.*, **22**, 261) heated the sub
nce in a nickel crucible with 10 drops of water and pure caustic potas
a water bath, stirring with a platinum wire, then gradually decom
ed the product with 0.5 to 1 gram of finely pulverized potassium
manganate, evaporated and drove out the precipitated carbon b
ition. The cooled crucible was brought into a warm dilute solutio
primary potassium sulphite, the solution acidified with acetic ac
n filtered into a silver nitrate solution. The silver halide was dete
ıed as usual. Or the cooled crucible might be put into water, th
ıtion acidified with acetic acid till the manganate is converted int
manganic acid, the latter destroyed with barium peroxide, the f
:d solution neutralized with primary sodium carbonate and the
ated. Robinson (*Am. Chem. J.*, **35**, 531) recommended a filling
combustion tube as usual with copper oxide, placing also in it a ca
lge filled with lead chromate, like Morse and Taylor's (*Ibid.*, **33**, 60
angement for the combustion of sulphur-bearing compounds. Va
and Scheuer (*Chem.-Ztg.*, **31**, 67) proposed to weigh out 0.2 to o
m of substance in a dry 150 to 200 cc. distilling flask, setting a se
tory funnel in place in the neck of the flask. The side arm was co
ted with a Volhard flask in such a way that it did not dip into th
er nitrate. 30 to 50 cc. of concentrated sulphuric acid were adde
stopper of the separatory funnel closed, the liquid warmed gradual
l a weak current of air passed through the apparatus either from th
inning or at the end of the experiment, according to the ease wi
ch the gases are evolved. Iodine was driven out of the side tu
warming. To insure the formation of silver iodide and not iod
ogen-free filter paper or metallic copper was placed in the distilli
k to increase the amount of sulphur dioxide formed. In the V
d flask silver halide and sulphite were formed, gathered into a beak
ıted with water and about 50 cc. of concentrated nitric acid, boil
sulphur dioxide was driven out or all silver sulphite was chang
ulphate, diluted till the sulphate dissolved and the halide determin
weighing or by titration of the silver in solution. Nitrogen ma
determined at the same time. Bianchi (*Boll. chim. farm.*, **45**, 82
icized this method, saying that it was not in general usable for c
ic chlorine derivatives; he did not pass on its value for bromine a
ne derivatives. If it does work for these it may be simplified
ıg the Volhard volumetric method. The Kjeldahl nitrogen dete
ation may be made at the same time all right.

as.—Franzen (*Ber.*, **39**, 2069) proposed the use of sodium hydr
hite for the absorption of oxygen, 1 gram absorbing 64 cc. of t
$Na_2S_2O_4 + H_2O + O = 2NaHSO_3$. 50 grams of the hydrosu
:e are dissolved in 250 cc. of water and 40 cc. of sodium hydroxi

solution (500 grams in 700 grams of water) and the solution used in a Hempel pipette for solid substances filled with iron wire gauze. 1 cc. of this solution absorbs 10.7 cc. of oxygen. It has the advantages of being cheaper than pyrogallol; it may be used in weakly alkaline solution and has the same absorption at various temperatures; it may be used with gases containing carbon monoxide (ammoniacal cuprous chloride cannot) and it may be used at lower temperatures and in the presence of substances that hinder the oxidation of phosphorus. For Bunte burette determinations a weaker solution is used which has to be shaken for three minutes. Haber (*Z. angew. Chem.*, **19**, 1418 and *Z. Elektrochem.*, **12**, 519) with Löwe had made by Zeiss a gas refractometer consisting of a prism telescope, a glass prism for the air or gas and a mirror. The observer looks at a luminous spot within the telescope. On looking into the instrument a dark shadow is seen which falls upon the scale in a position corresponding to the gas in the prism. The method has the advantage that the refractive index of the gas sample as compared with air remains the same as long as both are subjected to the same pressure and temperature changes. If chimney gases be led through the prism an increase of 0.9% carbon dioxide causes the image to be displaced 1 division of the scale. The instrument can be adapted for photographic registration or the shadow can be made visible at a distance. The apparatus is sensitive to 0.000,0003 in the refractive index, corresponding to a change of 0.2–0.25% carbon dioxide in chimney gases. Methane, hydrogen, hydrochloric and hydrocyanic acids can be determined in air with the same delicacy. The delicacy is twice as great for acetylene and hydrogen sulphide, 2½ times as great for sulphur dioxide and nearly 10 times as great for pentane and benzene vapor. Nowicki (*Oesterr. Z. Berg.-Hüttenw.*, **54**, 6) recommended oxidation with iodine pentoxide as the most satisfactory way to determine carbon monoxide, subsequently determining the carbon dioxide in various ways. Hydrogen sulphide is also easily oxidized. Acetylene acts on iodine pentoxide above 85°, but the carbon monoxide oxidation begins at 45° and is finished at 88°. The pentoxide heated by itself begins to decompose at 165° and the reaction is completed at 300°. Gautier and Clausmann (*Compt. rend.*, **142**, 485; *Bull. soc. chim.* [3] **35**, 513) made a similar recommendation with regard to carbon monoxide.

Soil.—Hall, Miller and Marmu (*Proc. Chem. Soc.*, **22**, 103; *J. Chem. Soc.*, **89**, 595) found that the commonly used moist oxidation with chromium trioxide yields always 10 to 20% too low values because the oxidation of the carbon does not proceed completely to the dioxide. They inserted a short layer of copper oxide. Murray (*Chem. News*, **93**, 40) used the following apparatus for the mechanical analysis of soils. An Erlenmeyer flask of about 200 cc. capacity without a flanged neck (neck of 2 to 3 cm. diameter) is bound to a piece of glass tubing of the same diameter as its neck by means of stout rubber tubing. 5 grams of fine, air-dried earth suspended in ammonia solution are put into the flask, it and the tube are filled carefully with water, the tube opening is closed and the apparatus turned upside down, the mouth being brought into a dish filled with water. Immediately under the tube opening is placed a small porcelain dish which is replaced by others at stated times. The portion deposited in each dish is evaporated and weighed. In order

to get a common basis for the expression of results Murray recommends uniting the particles that fall through 1 cm. in 1, then 5, 10, 20, 100 and 400 seconds.

Water.—Bruhns (*Z. anal. Chem.*, **45**, 473) stated that barium carbonate reacts alkaline and is attacked by dilute oxalic acid, hence the determination of carbon dioxide in water by precipitation with barium hydroxide and back titration with tenth-normal oxalic acid without filtering leads to errors. He used a tube carrying above a stopcock a cylindrical vessel of 100 to 300 cc. capacity and placed just above the stopcock glass wool or wadding and on top of that paper pulp, thus making a filter. The measured sample was put into this vessel and protected from air by a 3 to 5 mm. layer of benzene. The barium or calcium hydroxide solution was run in from a burette whose tip reached below the benzene layer. The mixture was carefully stirred, let stand to clear and the liquid run through the filter. The filtrate was caught under a 3 to 5 mm. layer of benzene and was titrated in small portions. Tenth-normal oxalic acid was used for titration and neutralized phenolphthalein for indicator if the water contained no magnesium. If ammonium chloride had to be added to keep magnesium in solution litmus or methyl-orange was used. It is not advisable to titrate under the benzene layer because acid can be occluded by it. Buisson (*Compt. rend.* **143**, 289 and *J. pharm. chim.* [6] **24**, 289) studied the determination of ammonia by Nessler's reagent. His analyses of the precipitate from ammonium chloride and the reagent lead to the formula $Hg_9N_4I_6$, agreeing with the work of François. The precipitate is soluble in potassium iodide, hence the reaction is reversible and some ammonia escapes detection (in one case 21%). The determination of ammonia carried out by determining the mercury in the precipitate is therefore inexact. Drawe (*Chem.-Ztg.*, **30**, 530) determined nitric acid by evaporating 100 cc. of water first with residue-free hydrochloric acid, then several times with water, then determining the chlorine in the solution of the residue. He subtracted from the total number of cc. of tenth-normal silver nitrate solution the number of cc. used in titration of the same amount of water sample and the number of cc. of tenth-normal acid combined in the determination of carbonate hardness in 100 cc. The difference was calculated to nitric acid. Kühn (*Arbl. kais Gesundheitsamt.*, **23**, 389) determined minimal amounts of lead by adding to 4 or 5 liters of the water a solution of 25 cc. of acetic acid and 500 cc. of sodium sulphide solution (8:500) mixed just before using. The coagulation of the colloidal lead sulphide was aided by the addition of 100 grams of sodium nitrate and the liquid was shaken with 2 grams of short fibered asbestos. The precipitate was filtered on asbestos, using suction, the lead sulphide oxidized by hydrogen peroxide containing a little nitric acid and the lead sulphate dissolved in sodium acetate solution. The rest of the method is that of Diehl and Topf (*Dingler's pol. J.*, **246**, 196; *Z. anal. Chem.*, **26**, 137, 277). It is accurate to 1 mg. of lead in 1 liter of water. Phelps (THIS JOURNAL, **28**, 368) determined small amounts of copper by evaporating 1 liter of the water to about 75 cc. (for 0.1 to 1 gram of copper), and adding 2 to 5 cc. of sulphuric acid and electrolyzing, using the dish as anode, with a current of $ND_{100} = 0.3$ ampere for 4 hours or over night with gentle stirring. The cathode was removed without interrupting the current

and dipped into boiled nitric acid. This solution was evaporated to dryness, the residue taken up in water, put into a 100 cc. Nessler tube, filled to the mark and 10 cc. of potassium sulphide solution (equal volumes of 10% caustic potash and saturated hydrogen sulphide solutions) added. The copper sulphide color appeared and was compared with the color in a similar tube of 10 cc. of the potassium sulphide solution diluted with water and standard copper sulphate solution added (0.2 cc. at a time) till colors were the same. For 1 liter of water taken, 1 cc. of the copper sulphate solution is equivalent to a copper content of 0.2: 1000000. Raschig (*Z. angew. Chem.*, **19**, 334) determined sulphuric acid by adding to the sample one-twentieth of its volume of a concentrated benzidine solution, stirring and allowing to stand 15 minutes. If there were no precipitate the water contained 1.5 mg. of sulphur trioxide per liter or less. The precipitate was washed by suction, using very little water, and titrated with tenth-normal sodium hydroxide (1 cc. = 4 mg. sulphur trioxide). There should be added for the benzidine loss 1.5 mg. Iron does not interfere if 1 to 2 cc. of a 1% hydroxylamine hydrochloride solution be added before the benzidine precipitation. Scriba (*Z. physik. chem. Unterricht*, **19**, 298) stated that a paper strip dipped in a solution of 1 gram of ferrous ammonium sulphate in 20 cc. of water, dried and rubbed with pulverized potassium ferricyanide will give a deep blue spot with the smallest amount of water.

Volumetric.—Acree and Brunel (*Am. Chem. J.*, **36**, 117) prepared a standard solution of hydrochloric acid by filling a clean liter flask nearly full of water, running through a single holed rubber stopper a glass tube with a long capillary reaching nearly to the bottom of the flask, weighing this to 0.001 gram with another flask as tare, then passing into it a current of dry hydrochloric acid gas till the increase in weight is a little more than 1 gram molecule. The flask is cooled to room temperature before the last weighing. The solution is then made up to the mark and the extra water added from a burette. A further standardization is unnecessary. Solutions of other gases obtainable dry, as hydrobromic and hydriodic acids, hydrogen sulphide, sulphur dioxide in any solvent, may be thus prepared. They gave also an improvement over the ordinary gravimetric method for standardizing hydrochloric or sulphuric acid solutions. About 4.12 grams of twice recrystallized primary sodium carbonate are neutralized with the necessary amount of acid (using methyl orange). The end point is reached when a weak rose-red color persists after some standing in a vacuum. The solution is evaporated to dryness in a weighed platinum dish and the residue heated to constant weight. From the weight of the sodium chloride or sulphate and the volume or weight of solution used it is easy to calculate the strength of acid. The method can be used with all acids, giving sodium salts that can be dried and weighed. Richardson (*J. Chem. Ind.*, **26**, 78) standardized sulphuric acid by neutralizing 5 cc. of dilute weighed acid with filtered saturated barium hydroxide solution, using phenolphthalein. The neutral solution was evaporated on the water bath and the barium sulphate ignited and weighed. Riegler (*Bull. assoc. chim. sucr. dist.*, **24**, 528) recommended ammonium triiodate [$NH_4H_2(IO_3)_3$] as an original standardizing material. For tenth-normal solution 3.025 grams of the salt are dissolved in 100 cc. of boiling

vater and this diluted to 1 liter. To standardize sodium thiosulphat
o cc. of water are put into a flask with 1 gram of potassium iodide, 1 cc
f hydrochloric acid (d. 1.2) and 10 cc. of the above triiodate solutio
nd the mixture titrated as usual with thiosulphate. $3NH_4H_2(IO_3)_3 +$
$Na_2S_2O_3 = 3Na_2S_4O_6 + 5NaIO_3 + NaI + 3H_2O + 3NH_4IO_3$. The tri
odate acts as a dibasic acid and so can be used directly for alkalimetr
vith luteol, Congo red or diazonitranilineguaiacol as indicator. Th
riiodate neutralized by sodium hydroxide is no longer affected by so
ium thiosulphate so the base to be determined can be treated wit
n excess of triiodate and the excess titrated back with thiosulphate
standardization of tenth-normal acid may also be effected gas volumetri
ally by letting the triiodate act on hydrazine sulphate and determin
ng the nitrogen (*Z. anal. Chem.*, **42**, 677). Wagner, Rink and Schultz
Chem.-Ztg., **30**, 1181) suggested the second method of Acree and Brune
or the standardization of acids and bases. They stated also that wher
here are tables showing the relation between refraction and concentra
ion the Zeiss immersion refractometer may be used to determine quan
itatively the reaction product. They gave a table for the relation be
ween refraction and concentration of nitric acid.

Ahlum (*Proc. Chem. Soc.*, **22**, 63; *J. Chem. Soc.*, **89**, 470) gave a volu
netric determination of free acid in the presence of iron salts, the iron bein
recipitated with monosodium phosphate, the phosphate filtered ou
nd the filtrate titrated with sodium hydroxide. The acid formed a
result of the iron precipitation, for example, $Fe_2Cl_6 + 2NaH_2PO_4 =$
$FePO_4 + 2NaCl + 4HCl$, is corrected for. Rupp (*Z. anal. Chem.*
5, 687) stated that permanganate oxidations run more rapidly an
igorously in alkaline than in acid solution, hence it is advisable in som
ases to oxidize in alkaline solution, then to acidify and titrate back th
xcess of permanganate according to Raschig (*Ber.*, **38**, 3911). Formi
nd nitrous acids are cases given as examples. The formate solutio
s warmed in a glass stoppered flask with considerable excess of perman
anate standardized against sodium thiosulphate and with 0.5 gra
f pure dry sodium carbonate for 15 to 30 minutes on the water bath
iluted after cooling with about 75 cc. of water, 25 cc. of dilute sulphuri
cid are added and 1 to 2 grams of potassium iodide, then the liberate
odine is titrated with tenth-normal thiosulphate (1 cc. = 0.0023 gra
f formic acid = 0.0023 gram of nitrous acid anion).

Brandt (*Z. anal. Chem.*, **45**, 95) found that the violet color of diphenyl
arbohydrazide (observed by Cazeneuve [*Chem.-Ztg.*, **24**, 684; *Bull. soc*
him. [3] **25**, 758]) could be used to detect the end point of the bichro
nate iron titration if a sufficient amount of hydrochloric acid were pres
nt with the manganese sulphate solution containing phosphoric acid o
he Reinhard method. There should be at least 60 to 80 cc. of hydrochlori
cid [d. 1.12] added to 1.5 liters of water containing 100 cc. of the manganes
olution (6 kg. of sulphate, 33 liters of dilute sulphuric acid [1 : 3] and 3 liter
f phosphoric acid [d. 1.7] diluted to 60 liters), the iron solution and th
ndicator (about 5 cc. of 0.1% solution). Then on titrating a red-viole
olor is obtained, becoming a mixed color as the green chromium salt in
reases till finally a sharp change to pure green is obtained at the end
Vithout the acid the decomposition of the coloring matter is too energeti
nd takes place before the iron is oxidized. Iron in amounts less tha

0.2 gram are to be titrated without the manganese sulphate solution which tends to weaken the oxidizing action on the coloring matter. With less than 0.1 gram ferric chloride must be added. Corsini (*Giorn. chim. farm.*, **55**, 200) recommended the use of tropaeolin OO in alcoholic solution as indicator in the determination of free mineral acids in bromatology instead of methyl violet. The color change from yellow to red-violet is sharper and more delicate than that of the latter, for example, for sulphuric acid 1:20000 (1:10000 with methyl violet) and for hydrochloric acid 1.5 to 2:2000 (2 to 2.5:1000). Fenton (*Proc. Camb. Phil. Soc.*, **13**, 298) stated that the previously described condensation derivative of methylfurfuraldehyde of the composition $C_{11}H_8O_4$ may be used as an indicator for strong acids and bases. A paper prepared from aqueous alcoholic solution gives with primary amines in acetic acid solution an intense green color destroyed by mineral acids; with urea in the presence of strong hydrochloric acid a blue color; with alkalies a violet-blue color destroyed by acids and disappearing on strong dilution. If the substance be melted at 120° with urea a colorless base is obtained giving a blue color with acids. Another acid indicator is obtained by boiling the compound with β-naphthylamine in alcohol solution which gives with weak acids an intense green color. Salm (*Z. Elektrochem.*, **12**, 99, and *Z. physik. Chem.*, **57**, 471) stated that by dilution of hydrochloric acid it is possible to prepare a series of standard solutions of varying hydrogen ion concentration. Solutions near the neutral point are better prepared by mixing tenth-normal monosodium and disodium phosphate solutions. For each one of these concentrations an indicator can be found which will give a color change. By comparison with suitably chosen standards the hydrogen ion concentration of solutions may be accurately determined, for example, for oxalic acid K = 0.09 (0.1), tartaric 0.0011 (0.00097), fumaric 0.0011 (0.00093) and camphoric 0.000,025 (0.000,0225). The figures in parentheses are from Ostwald's electrical conductivity measurements. The dissociation constant of an indicator base or acid is equal to the hydroxyl or hydrogen ion concentration of a solution half dissociated. With two-colored indicators like litmus such a solution is formed at the color change. With singly colored ones like phenolphthalein this solution is obtained by adding acid to the completely reddened liquid till the color intensity has half fallen away. The following dissociation constants are given:

Indicator acids.		Indicator bases.	
Methyl orange	$K = 4.6 \times 10^{-4}$	Cyanine	$K = 4.2 \times 10^{-6}$
p-Nitrophenol	2.3×10^{-7}	Dimethylaminoazobenzene	1.45×10^{-11}
Rosolic acid	1.1×10^{-8}		
Alizarin	8.8×10^{-9}		
Phenolphthalein	8.0×10^{-10}		

Indicators and color changes for definite hydrogen ion concentrations are:

Concentration of H^+.	Indicator.	Color change.
2N, 1N	Mauvein	Yellow-green
1×10^{-1}N	"	Green-green blue
1×10^{-2}N	"	Green blue-blue
1×10^{-3}N	"	Blue-violet
1×10^{-4}N	Congo red	Blue-violet

ncentration of H^+.	Indicator.	Color change.
1×10^{-6}N	Congo red	Violet-scarlet
1×10^{-6}N	Sodium alizarinsulphonate	Brown-red
1×10^{-7}N	Rosolic acid	Bright brownish red-rose
1×10^{-8}N	" "	Rose-red
1×10^{-9}N	Phenolphthalein	Colorless-rose
1×10^{-10}N	"	Rose-red
1×10^{-11}N	α-naphtolbenzoin	Green-green blue
1×10^{-12}N	Tropaeolin	Green yellow-orange
1×10^{-13}N	Trinitrobenzene	Colorless-orange
1×10^{-14}N	Benzopurpurin	Yellow(red)-rose
1×10^{-15}N	Safranine	Rose red-violet

Schoorl (*Chem. Weekblad*, 3, 719, 771, 807) defined color indicato
those coloring matters which possess distinctly different colors accor
g to whether the aqueous solution into which they are put contai
ee hydrogen or hydroxyl ions. In the first case they show "acid
lor, in the second, "basic" color. On transition from one color to th
her they show "transition" color. An acid delicate indicator is o
at shows transition color in aqueous solution that contains hydrox
ns, as phenolphthalein, tropaeolin OOO and curcumin; alkali delica
dicators are the opposite like *p*-nitrophenol, lacmoid, Congo and meth
ange and neutral indicators are those whose transition color show
aqueous solutions containing both ions, as rosolic acid and litmu
he different behavior of indicators in pure water is explained easi
the basis of the difference in their sensibility quotients H:OH; t
havior of solutions set at transition color on warming is explained
e change in that same quotient as a result of the increased dissoci
on of water molecules. The following results are given in a coup
tables:

Indicator.	Concentration of H^+	Concentration of OH^-	$H^+:OH^-$	Transition color.	Color in pure water at room temperature.	Color taken by so tion with transiti color on warmin
henolphthalein	10^{-9}	10^{-5}	10^{-4}	Bright red	Colorless	Colorless
opaeolin OOO	10^{-9}	10^{-5}	10^{-4}	Orange	Yellow	Yellow
urcumin.....	$10^{-7.5}$	$10^{-4.5}$	10^{-1}	Brown-yellow	Yellow	Unchanged
osolic acid....	10^{-7}	10^{-7}	1	Orange-red	Orange-red	"
tmus.....	10^{-7}	10^{-7}	1	Violet	Violet	"
Nitrophenol .	10^{-6}	10^{-8}	10^{2}	Clear yellow	Clear yellow	Intense yell
acmoid.....	10^{-6}	19^{-8}	10^{2}	Violet	Violet	Blue
ngo.....	10^{-4}	10^{-10}	10^{6}	Violet	Red	Red
ethyl orange..	10^{-4}	10^{-10}	10^{6}	Orange	Yellow	Yellow

ifferent values are obtained whether acid be titrated with alkali,
ce versa. This can be helped by titrating to the same end color
oth cases, for example, to clear red with phenolphthalein. Values
ined with methyl orange and phenolphthalein are not the same; t
fference can be decreased by titrating to the transition color in ea
se and neglected by titrating to the color of the indicator in water.

Optical.—Fredenhagen (*Ann. Physik* [4] **20**, 133) decided that t
ief series of the potassium and sodium lines are oxide spectra wh
e secondary series are due to the metals. The green thallium line
so an oxide line. He tried the alkalies and some other elements in t

ordinary, the carbon monoxide-oxygen and the hydrogen-chlorine flames. In the second flame the same spectra were observed for the alkalies as in the Bunsen flame. They gave no spectra in the hydrogen-chlorine flame, but when the chlorine was cut out the spectra appeared. Calcium and cuprous chloride gave chloride spectra in the hydrogen-chlorine flame. Riesenfeld and Wohlers (*Ber.*, **39**, 2628) found that an approximate quantitative determination of the alkaline earths can be made from the brilliancy of the lines of their spectra. With equal amounts the red and green calcium, the orange and blue strontium lines will appear equally bright but the two green barium lines are noticeably darker. With more than twice as much of any one, its lines will appear distinctly brighter. For detection of calcium and strontium the spectral analytical way is more delicate than the chemical, but for barium the chemical is better. A combination solution for the standardization of the spectral apparatus in one series of measurements may be made up of 50 cc. of water, 10 cc. of 10% hydrochloric acid, 1 drop of 10% sodium hydroxide, 10 grams of potassium chloride, 3 grams of strontium chloride, 1 gram of calcium chloride and 0.8 gram of lithium chloride. This gives the Kα, Liα, Na D, Caα, Srδ and Kβ lines.

Horn (*Am. Chem. J.*, **35**, 253) and Horn and Blake (*Ibid.*, **361**, 95, 576) stated that the assumption usually made in colorimetric work that the delicacy of all solutions which are more dilute than those obviously unsuited because of depth of color is practically the same, is not true. It is variable and the ease with which a determination can be carried out varies with the concentration, though a simple relation between them does not exist. Measurements with potassium bichromate solutions showed that the delicacy is greatest at concentrations of 0.004 to 0.008 normal calculated to gram atoms of chromium. The smallest amount of chromium that can be detected in distilled water is 0.000013 gram while 0.000001 gram causes an easily told difference at concentrations of maximum sensibility. The difference between depth of color of two colored solutions is much more easily detected than the difference between a colored and a colorless one. For colorimetric determinations the concentrations of greatest delicacy should be found experimentally and the conditions of experiment exactly laid down. The different amounts of potassium bichromate and of copper sulphate which cause a noticeable difference in color were determined. The reciprocals of these values plotted as ordinates with square roots of dilutions as abscissae gave a curve with two distinct maxima for the bichromate and one for copper sulphate. The copper sulphate curve corresponded to the first part of the bichromate curve. The delicacy of colorimetric analysis for copper is about thirty times as delicate as for chromium. The delicacy for copper sulphate is inversely proportional to the concentration of copper. Within certain concentrations the percentage errors are constant in all colorimetric analyses. The maximum of delicacy with ammoniacal copper sulphate lies at a concentration of 1 gram atom of copper in 4996.1 liters. In more concentrated solutions a change of 5 per cent. called forth a marked change in color. About the same relation was found to hold for ammonia-free copper sulphate (8 per cent.). The delicacy appears to be independent not of color tone but of the nature of the substance in solution.

De Vecchi (*Z. wiss. Mikrosk.*, **23**, 312) recommended 1 and 5 per ce methyl alcohol solutions of photoxyline as embedding material in croscopic work. Visser (*Chem. Weekblad*, **3**, 743) stated that inste of weighing the nitron precipitates in Busch's determination of nit acid they can be compared in height with precipitates from soluti of known content. Instead of 110 mg. per liter he found in this w 100 mg. Nitrous, chloric, perchloric, oxalic and salicylic acids g salts with nitron characteristic under the microscope. So also d saccharin after conversion with some drops of dilute alkali into *o*-sul aminobenzoic acid.

Analysis of Inorganic Compounds.

Noyes (*Techn. Quarterly*, **16**, No. 2; **17**, No. 3; *Chem. News*, **93**, 1 146, 156, 179, 189, 205, 216, 226, 239, 250, 262) has published part his system of qualitative analysis including practically all of the elemen It is worked out with great care with numberless test analyses, checks notes on the various procedures.

Metalloids, Oxygen, Sulphur.—Bancroft and Hamill (*J. Physiol* **34**, 306) determined the oxygen dissolved in physiological salt soluti by boiling the liquid under very low pressure (about 3 mm. of mercu and catching the gas in a 2 mm. wide tube. In such a tube 0.3 cc. gas will cause a bubble 100 mm. long. The analysis consists in not the difference in length of bubble before and after absorption with py gallic acid. Mathewson and Calvin (*Am. Chem. J.*, **36**, 113) gave a meth for the determination of hydrogen peroxide or of ferrous sulphate or ot reducing agents in which ferrous ammonium sulphate and ammonium s phate in about equal amounts are treated with 5 cc. of phosphoric a and diluted to 50 cc. Then 5 cc. of a titanium potassium sulphate lution are added and the titration carried out immediately with ab 0.15 normal hydrogen peroxide to yellow color. Results when the meth is reversed for hydrogen peroxide are a little lower than those of permanganate method which is to be expected because permangan oxidizes the organic matter of the hydrogen peroxide as well. W sodium nitrite the results are too high because the reaction is very s near the end point.

Berger (*Compt. rend.*, **143**, 1160) determined free sulphur by pou over an amount of substance containing 0.1–0.2 gram of free sulph 10 cc. of fuming nitric acid, adding 0.5 to 1 gram of potassium brom evaporating the liquid after a few minutes to dryness, fuming the- idue down 2 or 3 times with a few cc. of hydrochloric acid, taking up w water and precipitating as usual with barium chloride.

McFarland and Gregory (*Chem. News*, **93**, 201) detected sulp in crude iron by mixing 5 grams of sample intimately with 0.5 gram tartar, wrapping in filter paper and igniting for 15 minutes in a mu cooling, breaking up the mass, putting it in an evolution flask with tube dipping into an ammoniacal cadmium chloride solution. B ing hydrochloric acid (2 parts acid, 1 part water) is put on the mixt The solution containing the suspended cadmium sulphide is acidi with hydrochloric acid and titrated directly with normal iodine soluti Reinhardt (*Stahl u. Eisen*, **26**, 799) gave a similar method, treating iron sample with hydrochloric acid in an atmosphere of hydrogen catching the hydrogen sulphide in an ammoniacal cadmium solut

The precipitate was washed with ammonia, shaken with iodine solution, hydrochloric acid added, and the iodine titrated back with sodium thiosulphate and starch. Gyzander (*Chem. News*, **93**, 213) took up 0.2 gram of pyrites with a mixture of 5 cc. of hydrochloric and 15 cc. of nitric acids, evaporated, evaporated again with water and 5 cc. of concentrated hydrochloric acid, took up the residue with 100 cc. of water, 1 cc. of concentrated hydrochloric acid and 3 cc. of hydroxylamine hydrochloride solution (1 ounce in 500 cc. of water). After the iron was reduced the solution was heated to near boiling, 10 cc. of a cold 10 per cent. barium chloride solution added dropwise and the barium sulphate determined as usual. Hintz and Weber (*Z. anal. Chem.*, **45**, 31) took up their 0.5 gram of pyrites similarly, but removed the iron with ammonia, filtered and washed till filtrate and washwater amounted to 450 cc. This was neutralized, using methyl orange as indicator, 1 cc. of hydrochloric acid (d. 1.17) added, the whole heated to incipient boiling and precipitated with 24 cc. of 10 per cent. barium chloride solution diluted to 100 cc. heated to boiling and added all at once with vigorous stirring. The washed iron precipitate was dissolved in hydrochloric acid and precipitated again with ammonia, the filtrate and washwater from this treated again with barium chloride, any sulphate formed being added to the main quantity. Raschig (*Z. angew. Chem.*, **19**, 331) determined sulphur in pyrites by precipitation, after its oxidation, as benzidine sulphate, stating that the method is more accurate than Hintz and Weber's barium sulphate precipitation.

Bruhns (*Z. anal. Chem.*, **45**, 573) determined small amounts of sulphuric acid, especially in waters, by treating 150 cc. of the sample in a 200 cc. flask with 5 cc. of a barium chromate emulsion (29.45 grams of potassium chromate and 20 grams of primary potassium carbonate in 750 cc. of water with 48.86 grams of crystallized barium chloride in 250 cc. of water), pouring off the supernatant liquid and diluting the residual emulsion to 500 cc. 1 cc. of strong hydrochloric acid (3:2) was added and the whole allowed to stand with some shaking. Thirty minutes after the solution had colored yellow by solution of barium chromate in the hydrochloric acid it was made weakly alkaline with dilute ammonia, diluted to 200 cc. and filtered through a dry filter. After shaking, 100 cc. of the filtrate were treated in a glass stoppered flask with some potassium iodide and 5 cc. of hydrochloric acid (3:2) and after 30 minutes titrated with sodium thiosulphate and starch. Using twentieth-normal thiosulphate which has the value of thirtieth-normal here, the number of cc. used multiplied by 1.78 gives the number of mg. of sulphuric acid in 100 cc. of water. The result must be corrected by the subtraction of 0.15 cc. of thirtieth-normal thiosulphate. Johnson (THIS JOURNAL, **28**, 1209) determined carbon bisulphide in commercial benzene by conversion into copper xanthogenate, treating 75 cc. of benzene with 1 cc. of saturated alcoholic caustic potash for each 0.1 gram of bisulphide, adding a weighed amount of bisulphide (0.06 to 0.14 gram) and shaking for 15 to 20 minutes. The potassium xanthogenate was dissolved in water by shaking in a separatory funnel and the well washed benzene extracted with 3/4 of the original amount of caustic potash. The extracts and washwater were diluted to 500 cc., an aliquot portion weakly acidified with very dilute acetic acid and treated with copper

sulphate in not too great excess. This was allowed to stand for 1½ hours with repeated shaking, filtered and the precipitate washed, dried and ignited in porcelain. The results gave a $CuO:CS_2$ ratio varying from 1 : 1.593 to 1 : 1.825, an average of 1 : 1.750 or about 90 per cent. of Macagno's value 1 : 1.931. Seyewitz and Bloch (*Bull. soc. chim.* [3] **35**, 293) determined hydrosulphurous acid in hydrosulphites and their compounds with formaldehyde by means of their reduction of silver halides, $2AgCl + 4NH_3 + Na_2S_2O_4.2H_2O = 2NaCl + 2(NH_4)_2SO_3 + 2Ag$. Sulphites, bisulphites and hyposulphites do not do this. Hyraldite, $NaHSO_2.CH_2O.2H_2O$, decomposes smoothly with ammoniacal silver chloride at 80°. About 4 times the theoretical amount of silver chloride should be used.

Halogens.—Jannasch and Zimmermann and Jannasch alone (*Ber.*, **39**, 196, 3655) separated the halogens by adding to a solution of the mixture of their compounds in 120 to 150 cc. of water, 15 cc. of acetic acid and at least 3 cc. of 30 per cent. hydrogen peroxide and distilling off the iodine in 20 to 25 minutes in a current of steam. It was absorbed in hydrazine sulphate, concentrated ammonia and water. The contents of the absorption vessels were united, acidified with 30–40 cc. of nitric acid and precipitated cold with silver nitrate. The separation of chlorine and bromine is dependent upon concentration and upon presence of a determined excess of sulphuric acid. With much acid hydrogen peroxide sets bromine free even in the cold. It is separated by means of a current of carbon dioxide by mere warming on a weakly boiling water bath. Rupp and Horn (*Arch. Pharm.*, **244**, 405) gave a volumetric determination of iodine in the presence of chlorine and bromine ions. 0.2 to 0.4 gram of the substance was dissolved in 50 cc. of water, acidified with 25 cc. of dilute sulphuric acid and then about 3 grams of oxalic acid were added. 1 per cent. potassium permanganate was added till the liquid shaken upon flask wall showed a distinctly violet color, the mixture allowed to stand 3 hours with occasional shaking. 1 gram of potassium iodide was then added and the liberated iodine titrated with tenth-normal thiosulphate. In the presence of chlorine and bromine ions the end point of the permanganate addition fails. 10 cc. of 1 per cent. permanganate may be added when from 8 to 25 cc. of thiosulphate are required. Then by making a Volhard determination the data are at hand for iodine and chlorine ion separation, iodine and bromine or iodine from chlorine and bromine ions. Ville and Derrien (*Bull. soc. chim.* [3] **35**, 239) detected fluorine in food products by means of the fact that the absorption spectrum of methemoglobin is changed by sodium fluoride. The red band λ633 disappears and Menzie's band (λ612) appears. 100 cc. of red wine were evaporated ½ or ⅓ to remove alcohol, the volume made up again with water, 50 cc. of the liquid shaken with 1 gram of manganese dioxide, filtered, 25 cc. of the filtrate treated with 0.1 gram of dioxide, 1 to 1.5 cc. of defibrinated blood diluted with 4 volumes of a 1 : 100 solution of potassium oxalate added, shaken, filtered and tested. Or 100 cc. of the dealcoholized wine might be treated with 5 cc. of a solution of 1 part egg albumen and 7 parts of 1 per cent. potassium oxalate solution, the whole boiled up and filtered after cooling, 25 cc. treated with 1 to 1.5 cc. of the reagent blood and tested. Wines with 0.08 to 0.1 gram of sodium fluoride give Menzie's band.

Nitrogen, Phosphorus.—Bornwater (*Chem. Weekblad*, **3**, 30) gave a

simplified method for determining nitric acid in nitrates. He placed in an 800 cc. Erlenmeyer flask about 0.5 gram of nitrate, 200 cc. of bromine, 5 cc. of alcohol and 50 cc. of caustic potash (d. 1.3), also about 2.5 grams of finely cut aluminum wire. The flask was connected through tube and condenser with a vessel containing standardized sulphuric acid. It was heated slowly till the reaction started and to boiling only after the gas evolution weakened. Busch (*Z. angew. Chem.*, **19**, 1329) and Busch and Schneider (*Z. ges. Schiess.- u. Sprengstoffw.*, **1**, 232) determined the nitrogen content of nitrocellulose by warming 0.2 gram of sample in a flask with 5 cc. of 30 per cent. sodium hydroxide and 10 cc. of 3 per cent. hydrogen peroxide on a water bath and then boiling over free flame to complete solution. Forty cc. of water and 10 cc. more of 3 per cent. peroxide were added, the mixture warmed to 50° and 40 cc. of 5 per cent. sulphuric acid allowed to flow into the bottom of the dish from a pipette. The precipitation of the nitric acid was then made with nitron acetate. Busch (*Ber.*, **39**, 1401) determined nitrous acid by oxidation with warm neutral 3 per cent. hydrogen peroxide, acidification with 2 per cent. sulphuric acid and precipitation of the nitric acid formed as nitron nitrate (*Ibid.*, **38**, 861). Nitrous and nitric acids together may be determined by titrating the nitrous acid in an aliquot portion with permanganate and in another oxidizing it with hydrogen peroxide and weighing both acids as nitron nitrate. Reichard (*Chem.-Ztg.*, **30**, 790) stated that dry arbutin gives with as little as 0.0001 gram of nitric acid a yellow color. The color is fairly stable, especially if concentrated hydrochloric acid be used instead of concentrated sulphuric in the test. Forty per cent. caustic potash colors the solution reddish yellow, ammonia weak violet. Berberine and free nitric acid only on warming give a reddish brown substance, in great concentrations almost black, if hydrochloric acid be used to liberate the nitric acid. With sulphuric acid the reaction appears in the cold. It is more delicate than the first.

Artmann and Skrabal (*Z. anal. Chem.*, **46**, 5) determined ammonia iodometrically, treating the substance containing it with bromine and alkali, shaking in a closed flask, adding solid potassium iodide, acidifying and titrating the iodine with thiosulphate. Madri (*Gaz. chim. ital.*, **36** I, 373) criticized the method of Roberto and Roncali (*L'industria chimica*, **6**, 178) for the determination of hydrazine with permanganate. They stated that on heating, 5 molecules of nitrogen were set free for 4 molecules of permanganate. Madri said their own results never agreed with their own equation or with the earlier work of Peterson (*Z. anorg. Chem.*, **5**, 3). In acid solution the equation is, according to Peterson, $17N_2H_4.H_2SO_4 + 13O = 13H_2O + 7(NH_4)_2SO_4 + 10N_2 + H_2SO_4$. Without the acid the grade of oxidation of the hydrazine increases but does not reach the stage of Roberto and Roncali. Hence the reaction cannot be used for the determination of either permanganate or hydrazine. Potassium bichromate oxidizes hydrazine completely, as has been already pointed out by Purgotti (*Gaz. chim. ital.*, **26** II, 559).

Aronstein (*Chem. Weekblad*, **3**, 283, 493) detected white phosphorus in the presence of much phosphorus sesquisulphide by leading hydrogen or carbon dioxide mixed with air over the substance to be tested. Phosphorescence is given to the gas, disappearing as more air is blown

and appearing as the air content becomes again less. The pure s
iisulphide shows a similar behavior only at about 80° or above. T
st is delicate to 0.2 per cent. of phosphorus, if its absolute mass is
ss than 0.04 mg. He criticized Van Eijk's lead acetate method a
ated that rubbing the carbon bisulphide extract residue in the d
as delicate only to 1.4 per cent. of phosphorus in the sesquisulphi
an Eijk (*Ibid.*, **3**, 367, 404, 623) stated that a test tube containing
g. of phosphorus-free sesquisulphide would light up above 70° wh
e warmed at same time in the same water bath containing 0.02
nt. of phosphorus in the same amount of sesquisulphide would do
ider 60°. A better test is to distil the preparation with lead aceta
e sesquisulphide is decomposed and an illumination is observed w
02 mg. of phosphorus or more. To exclude red phosphorus it is
extract the mass with carbon bisulphide and to test the residue fr
aporation of the bisulphide for white phosphorus. If this extract
sidue be gently rubbed in a dark room, illumination is obtained in
esence of white phosphorus. The test is delicate to 0.004 mg.
esence of turpentine is disturbing to the phosphorus tests. An
ein's test is said to be less delicate than these. Schenck and Sch
ler., **39**, 1522) detected small amounts of white phosphorus by pa
g a current of air over the warmed substance and leading this to
otective cylinder of an electroscope. Phosphorus sesquisulph
uses scarcely any conductivity up to 75° and none at 50°, but a fr
on of a mg. of the white phosphorus will. Temperatures of 35°
° are the most suitable. The limit of sensibility is about 0.004
emens (*Arb. kais. Gesundheitsamt*, **24**, 264) tested the red phosphorus
mmerce for white or yellow by extracting 5 grams of the sample w
0 cc. of benzene on a boiling water bath for ½ hour by using a ret
ndenser. After cooling the filtered solution 1 cc. of it was trea
th 1 cc. of ammoniacal silver nitrate solution (1.7 grams of nitr
100 cc. of ammonia [d. 0992]) and shaken. If the color is weak
w there is no white phosphorus. The color is reddish or dark bro
there is a precipitate in its presence. In 1 cc. of benzene 0.01
white phosphorus can be detected. Mauricheau-Beaupré (*Com*
nd., **142**, 1206) gave a qualitative test for phosphorus. A piece
ass tubing 5 to 10 mm. in diameter is brought into the upper oxi
g part of a hydrogen or acetylene flame. In the presence of ph
orus the glass is not only etched but gains in weight, while with
osphorus it loses weight and there is no etching. The element m
terwards be determined in the etched part. Phosphine in acetyl
the ratio 1 : 10000 may be detected. Hydrofluoric acid must be
nt. Fricke (*Stahl u. Eisen*, **26**, 279) determined phosphorus in i
d steel by dissolving the sample in nitric acid, oxidizing the phospho
th permanganate, dissolving the precipitated manganese dioxide
mmonium chloride solution, evaporating to 30 or 40 cc., making wea
id by nearly neutralizing with ammonia and precipitating warm w
olybdate solution. The precipitate is filtered, washed with cold wa
l iron is removed, dissolved in standard sodium hydroxide solut
cc. = 0.00025 gram phosphorus) and the solution titrated back with
uric acid of the same strength using phenolphthalein. $2[(NH_4)_3PO_4.12Mo$
$46NaOH = 2(NH_4)_2HPO_4 + (NH_4)_2MoO_4 + 23Na_2MoO_4 + 22H$

$2P + 46NaOH = 23H_2SO_4$. Jannasch and Heimann (*Ber.*, **39**, 3625) stated that phosphoric acid can be quantitatively volatilized from its salts if an intimate mixture of phosphate and carbon be made first by treating phosphate and sugar solution in a distilling flask with sulphuric acid. The phosphorus is volatilized in a current of chlorine.

Arsenic, Antimony.—Berntrop (*Chem. Weekblad*, **3**, 315) determined the arsenic content of a mirror by oxidation at 60° with potassium bichromate and sulphuric acid. $5K_2Cr_2O_7 + 20H_2SO_4 + 6As = 5K_2SO_4 + 20H_2O + 5Cr_2(SO_4)_3 + 3As_2O_5$. The excess of bichromate is titrated back with potassium iodide and thiosulphate. The results are somewhat too low because of the formation of some arsenious oxide in the preparation of arsine in spite of efforts to keep air out and the retention of some arsine in the evolution flask, but chiefly because the liquid of the flask remains markedly arsenic-bearing. If this liquid be run again for arsenic and the result added to that of the main determination the method is good. Strzyzowski (*Pharm. Post*, **39**, 677) determined arsenic in animal objects, etc., by heating carefully in a porcelain crucible, 1 gram of magnesia, 10 cc. of the liquid (5 to 10 g. of half solid matter or 1 gram of solid broken up and rubbed with 10 cc. of water) and 0.5 to 1 cc. of concentrated nitric acid on an asbestos plate, then over a free flame till after breaking up the residue is pure white. This is taken up with 10 cc. of water and 5.5 cc. of 50 per cent. sulphuric acid, filtered from the calcium sulphate and carbon, and the filtrate brought by washing with 12½ per cent. sulphuric acid to 20 to 25 cc. and the magnesium arsenate in solution investigated in the author's Marsh test apparatus. Rosenthaler (*Z. anal. Chem.*, **45**, 596) determined arsenic acid by the reverse of the iodometric method for arsenious acid. $2H_3AsO_4 + 4KI + 4HCl = As_2O_3 + 4I + 4KCl + 5H_2O$. The reaction is complete at the end of 10 to 15 minutes and the liberated iodine is titrated as usual. Both acids of arsenic may be determined by obtaining the arsenious acid amount first and after oxidation the total amount of arsenic acid.

Low (THIS JOURNAL, **28**, 1715) gave a technical determination of arsenic and antimony in ores in which the sample is taken up with primary potassium sulphate, tartaric and concentrated sulphuric acids. The two sulphides are precipitated by hydrogen sulphide from this diluted and filtered solution, then they are dissolved in potassium sulphide solution. This solution is evaporated with primary potassium sulphate and concentrated sulphuric acid and finally heated till the sulphur and most of the free acid are gone, the cooled residue taken up with water and concentrated hydrochloric acid and the arsenic precipitated with hydrogen sulphide. The filtrate is evaporated again with primary sulphate and sulphuric acid, the cooled residue taken up with water and hydrochloric acid, diluted and titrated with permanganate. The oxalic acid value of the permanganate solution multiplied by 0.9532 gives the antimony value. The arsenic precipitate is dissolved in water containing ammonium sulphide, the solution evaporated with primary sulphate and acid, and the cooled melt taken up with water and boiled. The solution is made weakly alkaline with ammonia, then acid with hydrochloric acid, cooled to room temperature, primary sodium carbonate added and the solution titrated with iodine. Materne (*Bull. soc. belg. chim.*, **20**, 46) separated arsenic, antimony and tin by treating the sul-

phide mixture (containing bivalent tin without tetravalent) with a hot 2 per cent. borax solution, filtering and washing with gradually decreasing strength of borax solution; the filtrate contained the arsenic. The precipitate was treated with boiling 5 per cent. sodium carbonate solution and filtered hot; the filtrate contained antimony. The tin in the residue was dissolved in 10 per cent. sodium hydroxide. If stannic tin were present instead of stannous, the arsenic was removed by digestion with cold 2 per cent. borax solution and the residue boiled with 5 per cent. sodium hydroxide solution, dissolving out the tin; the antimony in the residue could then be dissolved in hot 5 per cent. sodium carbonate solution. Treatment of these solutions with hydrochloric acid or with tartaric acid and ammonium chloride gives the sulphide in each case. The borax solution is made up of 500 cc. of 2 per cent. borax and 20 cc. of 10 per cent. ammonium chloride, the sodium carbonate solution of 500 cc. of 5 per cent. sodium carbonate and 10 cc. of 10 per cent. ammonium chloride, and the tartaric acid solution of 300 cc. of 20 per cent. acid and 150 cc. of 10 per cent. ammonium chloride. Czerwek (*Z. anal. Chem.*, **45**, 505) separated antimony from tin in alloys by dissolving in a warm mixture of tartaric and concentrated nitric acids with a little water and precipitating the tin from this solution heated to incipient boiling by 45 per cent. phosphoric acid. The precipitate was filtered, washed with dilute ammonium nitrate solution, dissolved in warm ammonium sulphide, reprecipitated with dilute sulphuric acid, filtered, washed again with dilute ammonium nitrate, dried and ignited to tin dioxide, oxidizing with nitric acid. The filtrate was neutralized with ammonia, ammonium sulphide added, the solution acidified with acetic acid and the antimony trisulphide filtered warm. The precipitate was washed with dilute ammonium nitrate, dissolved in a large porcelain crucible with ammonium sulphide, the solution evaporated, the residue oxidized with fuming nitric acid and ignited to antimony tetroxide. With other metals present the tin phosphate was washed with 150 to 200 cc. of hot normal nitric acid, dissolved in ammonium sulphide, or sodium sulphide if copper were present, and the tin precipitated as above. In the tin filtrate other metals were removed with ammonia and ammonium sulphide and the antimony precipitated by acetic acid.

Carbon, Boron, Silicon.—Aupperle (THIS JOURNAL, **28**, 858) gave a volumetric method for the determination of carbon in iron and steel which rests on the titration of barium hydroxide into which the carbon dioxide from the combustion of filings of the sample in oxygen has been passed. He stated that the barium hydroxide may be titrated with acid in the presence of barium carbonate without losing carbon dioxide if the acid be run deep into the solution by means of a long capillary tube for any dioxide set free is absorbed again by the hydroxide above. (Cf. Bruhns, p. 426 *Super.*) Rosenthaler and Türk (*Arch. Pharm.*, **244**, 517) and the former alone (*Ibid.*, **244**, 535) investigated the percentage of dissolved substance absorbed from 1 per cent. solutions of it in different solvents by 5 times its weight of different kinds of charcoal in the cases of codeine, caffeine, salicine, picrotoxine, gallotannic, gallic and oxalic acids, potassium oxalate, indigotine and glucose. The amount and rate of adsorption are greatest in the case of animal charcoal, great also with "flesh"

and less so with "plantblood" charcoals, and are small with "blood," "limewood" and "sponge" charcoals. They are greatest in aqueous solutions, then in descending order come ethyl alcohol, methyl alcohol, acetic acid, acetone and chloroform. There is relatively less adsorbed in concentrated than in dilute solutions. Adsorption and decolorization are little dependent on the temperature. The more readily a substance is adsorbed the more difficult it is to dissolve it out again. The decolorizing power of charcoals is dependent on their adsorbing power. Charcoal to be used for decolorizing should be carefully purified and used in as small amount as possible. Solutions in solvents other than water and as concentrated as possible are advisable. Substances readily oxidizable must not be decolorized with animal charcoal. The percentage of a substance adsorbed increases with its molecular weight. Coloring matter in a solution usually has a high molecular weight and its concentration in the solution is usually small, both being conditions favorable to adsorption.

Castellana (*Gaz. chim. ital.*, **36** I, 136, 232) stated that the green flame test for boric acid is obtained if the substance be mixed with potassium ethyl sulphate and heated with the flame till the first vapors rise and then setting fire to these. 0.5 mg. of boric acid may be detected. The characteristic odors of their esters are obtained with a considerable number of organic acids if carefully heated dry with potassium ethyl sulphate. He stated in reply to Velardi's (*Ibid.*, **36** I, 230) criticism that copper chloride, phosphites and hypophosphites do not interfere with the boric acid color and that the turmeric paper test is not superior to his in delicacy. Fendler (*Z. Nahr.-Genussm.*, **11**, 137) gave a modification of the turmeric paper test, comparing the color obtained under certain conditions with a variety of standard colors obtained with known amounts of boric acid. Low (THIS JOURNAL, **28**, 807) found that the turmeric test is extraordinarily sharp if the paper be dried not at 100° but at ordinary temperatures or 40° to 50° in a vacuum desiccator. In 1 cc. 0.000,001 gram of boric acid may easily be detected. In the quantitative determination it is not possible to drive all of the boric acid out of water solution with methyl alcohol because the smallest amount of water will hold back considerable acid. All the acid may be driven over by the use of some water-extracting substance like calcium chloride.

Hinden (*Z. anal. Chem.*, **45**, 332) said that the taking up of silicates after evaporation with hydrofluoric acid may be accomplished by evaporating 4 to 6 times with hydrochloric acid, the bases being converted into chlorides. One gram of substance is moistened in platinum with a little water and evaporated down with 10 to 15 cc. of concentrated hydrofluoric acid, the residue taken up with hydrochloric acid (1:1), 10 cc. of hydrofluoric acid again added, evaporated and the evaporation repeated about 6 times with 10 to 20 cc. of hydrochloric acid. Complete decomposition is not to be obtained in this way with barium and lead-bearing glasses; here the recommendation is made to filter off the insoluble residue and to treat again with the two acids. Schucht and Möller (*Ber.*, **39**, 3693) titrated hydrofluosilicic acid with sodium hydroxide in the presence of methyl orange, adding first an excess of neutral calcium chloride solution. $H_2SiF_6 + 3CaCl_2 + 6NaOH = 3CaF_2 + 6NaCl + H_4SiO_4 + 2H_2O$.

Metals, General.—Tarugi and Marchionneschi (*Boll. chim. far*
, 629) gave some particulars regarding the use of thioacetic acid reco
:nded by Schiff and Tarugi (*Gaz. chim. ital.*, **24**, 551) in qualitat
alysis. They stated that it works well. Under pressure in sea
ɔes at 90° it gives complete precipitation of sulphides much m
ıdily than hydrogen sulphide, and in acid concentrations such t
der normal circumstances no sulphides would form. The act
thioacetic acid in closed vessels at 90° is equal to that of hydro
phide at 14.34 atmospheres. Daitz (*Z. anal. Chem.*, **45**, 92) cr
ed the ammonium sulphide group separation of Boetticher (*Ib*
99), saying that in the separation of cobalt, nickel, iron and man
se from aluminum, zinc and chromium by excess of sodium hydr
and bromine a good deal of nickel and some cobalt go into soluti
o that on treatment of the first four as hydroxides with concentra
drochloric acid, evaporation, addition of excess of ammonia, heat
boiling after strong shaking and addition of 2 to 3 cc. of hydro
'oxide and filtering, much nickel and some cobalt are left in the r
: while a good deal of iron and manganese go into the filtrate wh
ıuld contain only complex nickel and cobalt salts. Jannasch a
imann (*J. pr. Chem.* [2] **73**, 473, 488) gave some more metal sepa
ns by distillation in a current of dry hydrochloric acid gas. Tin c
over away from cadmium at a temperature not above 320°. E
th is separated from cadmium by distilling at temperatures betw
›° and 350°; bismuth and silver may be easily separated. Antimo
tils from lead mixture between 150° and 250°. Antimony a
ıper, cadmium or silver may be separated. The temperat
:d in no case exceed 350°. The authors upheld their method agai
edheim's (*Z. anal. Chem.*, **44**, 465) criticism.

Alkalies.—Hübener (*Chem.-Ztg.*, **30**, 58) in detecting sodium sulph
thiosulphate made use of the fact that the sulphur dioxide liberat
m the thiosulphate requires twice as much iodine for its oxidati
does the thiosulphate itself. $Na_2S_2O_3.5H_2O + I = \frac{1}{2}Na_2S_4O_6 + NaI$
$_2O$. $Na_2S_2O_3.5H_2O + H_2SO_4 = SO_2 + S + Na_2SO_4 + 6H_2O$. SO
$+ H_2O = 2HI + H_2SO_4$. One determination is made direct, w
ine, another by passing the sulphur dioxide evolved in an atmosph
ɜarbon dioxide through an excess of iodine and titrating back. Th
› values by suitable calculation give the amounts of sulphite a
ɔsulphate in the sample. He found in a sample supposedly 90 p
t. pure, 92.87 per cent. thiosulphate, 3.11 per cent. sulphite and 2.
cent. sulphate, the last figure representing sodium sulphate cor
nding to the barium sulphate difference of the totally oxidized sa
and that calculated to correspond to the sulphite and thiosulpha
mimboeuf (*Ann. chim. anal. appl.*, **11**, 130) determined potassi
ɔride in potassium bromide by precipitating both as silver salt a
ghing. 2 grams of pure potassium bromide should give 3.15
ms of silver bromide while 2 grams of potassium chloride should wei
;23 grams as silver chloride. He assumed 1 per cent. of potassi
ɔride would increase the weight of the silver bromide by 0.0069
n and gave a table for the chloride content of the bromide. Paje
z. *chim. ital.*, **36** II, 150, 298) stated that the solubility of potassi
ɔotassium and sodium persulphate is increased by the presence

sodium sulphate and decreased by potassium sulphate, the solubility coefficients per 100 cc. at 12° being for saturated solutions of sodium sulphate 5.982, of primary sulphate 8.72, of potassium sulphate 0.792, of primary sulphate 0.329. There is direct proportionality to the greater or less solubility of the sodium or potassium salt. The solubility of the persulphate in sodium salt solutions is a function of their concentration of sodium. Hence the greater solubility in the presence of sodium salts is probably due to chemical action. $K_2S_2O_8 + Na_2SO_4 = Na_2S_2O_8 + K_2SO_4$. On this ground he criticized Tarugi's (*Ibid.*, **34** I, 324) method for the determination of potassium. Schlicht (*Chem.-Ztg.*, **30**, 1299) observed that sodium phosphomolybdate solution gives a yellow precipitate when heated with potassium salts acidified with nitric acid and makes a good test for potassium.

Beryllium, Magnesium, Alkaline Earths.—Glassmann (*Ber.*, **39**, 3366, 3368) gave a quantitative separation of beryllium and aluminum, neutralizing the hydrochloric or sulphuric acid solution of the oxides approximately with sodium carbonate and adding excess of sodium thiosulphate, then boiling till the odor of sulphur dioxide disappears and heating for ½ hour on the water bath. Beryllium remains in solution as sulphite or basic sulphite. The aluminum hydroxide and sulphur precipitate is washed and ignited. The excess of thiosulphate in the filtrate is decomposed with hydrochloric acid and the beryllium precipitated with ammonia or according to Glassmann's method with potassium iodide and iodate, which according to Friedheim (*Ibid.*, **39**, 3868) was first described by Joy in 1864 and later by Zimmermann in 1887. Parsons and Barnes (THIS JOURNAL, **28**, 1589) separated beryllium from aluminum and iron by neutralizing the chloride solution as nearly as possible with ammonia, treating the cold solution with 10 grams of primary sodium carbonate, heating the mixture as rapidly as possible to boiling and boiling for 1 minute. The beaker is set in cold water to cool, the precipitate filtered and washed with hot water and dissolved on the filter in as little hydrochloric acid (1:1) as possible, diluting to 100 cc. in the original beaker. This solution is neutralized with ammonia and the precipitation repeated. The filtrate and washings are neutralized with concentrated hydrochloric acid, the precipitate dissolved, the solution boiled to drive out carbon dioxide and the beryllium precipitated by ammonia as the hydroxide, this washed with ammonium acetate solution, dried, ignited and weighed as the oxide. The aluminum hydroxide precipitated is dissolved in hydrochloric acid, reprecipitated with ammonia, ignited and weighed. The iron separation is the same.

Grimbert (*J. pharm. chim.* [6] **23**, 237) carried out the Schlagdenhauffen reaction for magnesium by treating 10 cc. of the solution with 5 cc. of 10 per cent. potassium iodide and 2 to 3 drops of a concentrated sodium hypochlorite solution. In the presence of magnesium a reddish precipitate looking like ferric hydroxide is obtained. The test is delicate to 1:2000; the solution must never be acid. Bellier (*Ibid.*, [6] **23**, 378) treated the magnesium solution with a solution of iodine in potassium iodide and then dropwise with dilute sodium hydroxide. With more than 0.02 per cent. of magnesium a relatively abundant reddish brown precipitate is obtained; with 0.005 per cent. a reddish brown-yellow color. A delicacy of 1:20000 is claimed for this modification.

Ammonium salts, acids and alkalies prevent the reaction completely; lime lowers its delicacy somewhat. The precipitate is perhaps a mixture of magnesium oxide and iodine. Berju (*Chem.-Ztg.*, **30**, 823) determined small amounts of magnesium indirectly by weighing the phosphoric acid of magnesium ammonium phosphate as $P_2O_5.24MoO_3$.

Löb (*Ibid.*, **30**, 1275) found that barium dioxide could not be titrated with permanganate in the presence of sulphuric acid because the barium sulphate apparently occluded some of the substance, but it might be in the presence of hydrochloric acid and manganese sulphate. The results of the method were compared with those of an iodometric one, the barium dioxide in hydrochloric acid solution being treated with potassium iodide solution and the iodine titrated back with thiosulphate. A neutral or weekly ammoniacal solution of the alkaline earth was treated by Benedict (THIS JOURNAL, **28**, 1596) with its volume of 5 times normal hydrochloric acid, then 2 to 3 cc. of saturated potassium iodate solution. No precipitate indicates the absence of barium, an immediate one shows considerable and a slow one little barium or considerable strontium. The filtrate is tested with a little more than an equal volume of saturated ammonium sulphate solution and heated to boiling; a white permanent precipitate indicates strontium. Another portion of the original solution is allowed to stand with twice its volume of saturated potassium iodate solution for ½ to 1 minute after shaking, then the filtrate is tested with ½ its volume of ammonium oxalate for calcium. Caron and Raquet (*Bull. soc. chim.* [3] **35**, 1061) precipitated barium as chromate from the alkaline earth mixture, then after making the filtrate alkaline again with ammonia threw out the strontium with alcohol. The calcium was tested for with potassium ferrocyanide solution.

Iron, Aluminum.—Komar (*Chem.-Ztg.*, **30**, 15, 31) obtained the salt $FeH(SO_4)_2.4H_2O$ by evaporation of a solution of ferric sulphate (prepared by the oxidation of a solution of ferrous sulphate in sulphuric acid by means of nitric acid or by electrolysis) from a sulphuric acid content of 400 cc. of the monohydrate per liter to a concentration of 45° to 50° Baumé. The compound is partly easily soluble in water, partly difficultly. The at first cloudy and finally clear green solution reacts weakly acid and does not reduce permanganate. By heating at 90° to 100° the compound destroys paper and smells of sulphuric acid; on gently heating in a crucible sulphur trioxide and ferric oxide are obtained. Iron and zinc may be separated by conversion into sulphates, dissolving these in sulphuric acid (400 cc. of monohydrate per liter [d. 1.3 to 1.4]), evaporating this solution to dryness and igniting the residue to constant weight over the burner. The zinc sulphate decomposes only at about 700° and may be extracted with water. Rupp and Horn (*Arch. Pharm.*, **244**, 571) modified Rupp's (*Ber.*, **36**, 164) method for the titration of ferrous salts with alkali hypoiodite, using caustic potash in place of sodium potassium tartrate as the hydriodic acid binding agent. Ferrous iron is instantly oxidized to ferric by the measured excess of tenth-normal iodine in the presence of normal or 5 per cent. caustic potash. The solution is then acidified with acetic or better with oxalic acid and the iodine excess titrated with thiosulphate.

Moody (*Am. J. Sci.* [4] **22**, 483; *Z. anorg. Chem.*, **52**, 286) gave an

iodometric determination of basic alumina and free sulphuric acid in aluminum sulphate and alums. The iron is determined in aliquot portions before and after reduction with zinc, and any zinc by electrolysis from acetate solution. A portion is boiled with potassium iodide-iodate mixture in a suitable apparatus and the iodine collected in a receiver containing potassium iodide. After slightly acidifying with sulphuric acid the iodine is titrated with thiosulphate. The precipitate formed in the flask contains besides alumina, ferric and zinc oxides which are determined in the usual ways. 1 molecule of alumina requires 6 atoms of iodine, 1 of ferric oxide 6 of iodine, 1 of ferrous oxide 2 of iodine, 5 of zinc oxide 8 of iodine, 1 of ammonium 1 of iodine and 1 of sulphuric acid 2 of iodine. The decomposition of zinc sulphate is abnormal. $15ZnSO_4 + 20KI + 4KIO_3 + 12H_2O = 3Zn_5(OH)_8SO_4 + 12K_2SO_4 + 24I$. The total iodine less the sum calculated to correspond to the single sulphates gives the iodine difference; if this be positive the mixture contains free acid, if negative, free alumina.

Cobalt, Nickel, Manganese, Zinc.—Alvarez (*Ann. chim. anal. appl.*, 11, 445; *Chem. News*, **94**, 306) stated that the blue color pointed out by Donath in 1901 as obtained when solid caustic potash or soda or very concentrated alkali solution was added to cobalt solutions is obtained also when barium hydroxide, calcium chloride or other water-extracting substance is added. 1 drop of 1:100 cobalt solution added to boiling concentrated alkali solution will give the reaction, which takes place in the presence of nickel. Grossmann and Schück (*Ber.*, **39**, 3356) gave a new test for nickel, treating a solution of dicyanodiamine with a little hydrochloric acid, heating to boiling, adding the nickel salt, then caustic potash solution and obtaining a yellow crystalline precipitate of nickel dicyanodiamidine ($Ni[C_2H_5ON_4]_2.2H_2O$) in needles arranged in star shapes. They are immediately soluble in potassium cyanide, but not in boiling caustic potash solution, and are sparingly soluble in water and ammonia. Cobalt forms no analogous compound. Reichard (*Chem.-Ztg.*, **30**, 556) stated that if powdered dehydrated nickel salts of mineral acids are heated with an equal amount of fully dry methylamine hydrochloride in porcelain the color becomes deep dark blue. This color disappears on cooling, leaving a dirty gray-yellow, solid mass which soon deliquesces. It becomes blue again on heating and decolorizes on cooling. The color is shown with 0.1 mg. of nickel. Cobalt salts similarly heated yield deep blue oily drops which do not lose their color on cooling.

Funk (*Z. anal. Chem.*, **45**, 562) observed that iron and manganese sulphides dissolve very easily in dilute acids, but in the presence of ammonium salts nickel sulphide and even more easily cobalt sulphide dissolve, too. At ordinary temperature nickel and cobalt sulphides are not dissolved by a little dissociated acid like formic but in separations they dissolve and some iron sulphide remains. Manganese sulphide dissolves except for traces. Jannasch and Gottschalk (*J. pr. Chem.* [2] **73**, 497) precipitated manganese from ammoniacal solutions by means of oxygen rich in ozone. Small amounts of manganese can be precipitated by slow passage of the ozone through the ammoniacal solution. Large amounts are managed by adding the manganese solution dropwise to 100 cc. of strong ammonia through which a vigorous ozone current is

passing. The precipitate is hydrated manganese dioxide. Manganese may be separated from sodium, calcium and zinc in this manner by one precipitation. Magnesium, nickel, cadmium and copper each require a repetition of the precipitation in order that the manganese may be free from them; the precipitate is dissolved in hydrochloric acid containing hydrogen peroxide. The separation of manganese and cobalt failed. Tarugi (*Gaz. chim. ital.*, **36** I, 332) gave a test for manganese and a new method for the formation of glycerose. Manganese hydroxide dissolves in glycerol and such a solution colors itself red by oxidation through air or more quickly through oxygen or sodium hypochlorite. The color intensity depends only on the amount of manganese present. 0.00001 gram of manganese can be detected. Cobalt and copper interfere only with amounts of less than 1 per 1000. Glycerol is converted into glycerose through sodium hypochlorite by 1 drop of 1:1000 cobalt chloride solution. 50 cc. of glycerol, 2 cc. of 5.9:1000 cobalt chloride and 10 cc. of 50 per cent. caustic soda put all at once into 150 cc. of sodium hypochlorite (7 per cent. active chlorine) gave on cooling in ice, 18 per cent. of glycerose.

Bertrand and Javillier (*Compt. rend.*, **143**, 900; *Bull. soc. chim.* [4] **1**, 63) gave a method for the precipitation of zinc, treating a solution containing zinc and a sufficient amount of lime with excess of ammonia and heating to boiling, the calcium zincate coming out in microscopic crystals. It is difficultly soluble in excess of lime and may be used for quantitative work. The zincate is mixed with carbonate; the precipitate is dissolved in hydrochloric acid, the solution evaporated to dryness, the residue taken up with some water, the lime precipitated with ammonium oxalate and the filtrate evaporated and ignited with sulphuric acid to zinc sulphate. Less than 1 part of zinc in 500,000 of solution can be detected. A zinc test was given also by Bradley (see under copper).

Mercury, Silver.—Rupp (*Ber.*, **39**, 3702) gave a volumetric determination of mercury, adding to the mercuric salt solution (about 0.2 gram in 25 to 50 cc.) 1 to 2 grams potassium iodide so that the precipitate first formed dissolves, making alkaline with caustic potash or soda, then adding with shaking, a mixture of 2 to 3 cc. of 40 per cent. formaldehyde and 10 cc. of water. The mixture is acidified with acetic acid to distinct odor, an excess of tenth-normal iodine solution (25 cc.) added, the metallic mercury brought into solution by shaking and the excess of iodine titrated with tenth-normal thiosulphate. Utz (*Pharm. Post*, **39**, 785) modified his 1905 method of determining sublimate in dressing materials to conform to this mercury determination of Rupp's. Seidell (THIS JOURNAL, **28**, 73) determined mercury and iodine in antiseptic soaps by treating the soap sample with 150 cc. of 95 per cent. alcohol and 3 to 5 cc. of concentrated hydrochloric acid, warming the mixture and adding gradually small amounts of water till the whole is in solution. Mercury is precipitated as sulphide, filtered into a Gooch crucible and washed with 95 per cent. alcohol. The filtrate freed from fat may be shaken in a separatory funnel with chloroform and a few drops of nitrous acid and the iodine in the chloroform determined by titration with thiosulphate. Goldschmidt (*Z. anal. Chem.*, **45**, 87) stated that silver is precipitated quantitatively as a black powder, if cobalt foil be put into

boiling silver salt solutions and that it may be weighed. Gold is likewise thrown out of boiling solutions by nickel as a brown powder.

Copper, Cadmium, Bismuth.—Bradley (*Am. J. Sci.* [4] **22**, 326) observed that the blue color of "logwood hematoxylin" and copper salts is a copper test of extraordinary delicacy, 1 : 1000,000,000. Zinc nitroprusside is crystalline and may be detected under the microscope even in the presence of amorphous precipitates, the reaction being much more delicate than the common precipitation tests for zinc. Rhead (*Proc. Chem. Soc.*, **22**, 244; *J. Chem. Soc.*, **89**, 1491) determined copper with the aid of standard titanium trichloride solution in the presence of potassium thiocyanate. Cupric salts are reduced and the copper precipitated in the presence of sulphuric or hydrochloric acid as cuprous thiocyanate. A ferrous salt is added to sharpen the end-point. The cupric salt oxidizes an equivalent amount of the ferrous salt and the red color of ferric thiocyanate appears. The color disappears at the end of the reaction. The titration must be carried out below 30° and as rapidly as possible. Nitric acid must be absent. Ferric iron and cupric copper may be determined together and the iron subtracted after separate determinations. The titanium trichloride is standardized by means of a ferric salt solution obtained by the oxidation of a ferrous salt with permanganate.

Goldschmidt (*Z. anal. Chem.*, **45**, 344) observed that cadmium is quantitatively precipitated from boiling salt solutions in aluminum dishes in the presence of traces of chromium and cobalt nitrates. The catalyzing agent is aluminum. Other metals can be used for the quantitative determination by catalysis. Moser (*Ibid.*, **45**, 14) found that bismuth precipitated as phosphate would carry down some cadmium in the separation of bismuth from copper and much cadmium and that the cadmium is hard to remove. It is not easy to make a second precipitation of the bismuth phosphate because of its insolubility. The method is good for the determination of bismuth alone but as a separation has no advantages over the ordinary one.

Uranium, Vanadium, Molybdenum, Tungsten.—Finn (THIS JOURNAL, **28**, 1443) separated uranium and vanadium, after solution of the mineral sample in sulphuric acid, by precipitating twice with excess of sodium hydroxide solution, boiling each time, acidifying the united filtrate and washwaters with sulphuric acid, adding ammonium phosphate and making alkaline with ammonia. The filtrate containing vanadium is acidified with sulphuric acid, reduced with sulphur dioxide till the solution is blue and titrated hot with permanganate. The uranium precipitate ($UO_2NH_4PO_4$) is dissolved in sulphuric acid reduced with zinc and the filtrate titrated with twentieth-normal permanganate at 60°. The iron factor multiplied by 1.631 gives vanadium pentoxide, by 0.9159 vanadium, by 2.567 uranous uranic oxide and by 2.133 uranium. Gilbert (*Z. öffentl. Chem.*, **12**, 263) determined molybdenum in glance by extracting the trioxide with ammonia, after roasting in air, and igniting to constant weight. The small amout of molybdenum left in the roasted ore is obtained by fusing with potassium and sodium carbonates, taking up with acid, reducing with zinc and titrating with permanganate.

Von Knorre (*Stahl u. Eisen*, **26**, 1489) modified his earlier method for determining tungsten in steel. The steel is dissolved in hydrochloric

cid with exclusion of air and without filtering the
zed with sodium carbonate; after cooling, 10 cc. of appr
ormal sulphuric acid or alkali sulphate and 40 to 60
olution are added. The precipitate of tungsten, ben
nd sulphate is filtered, washed with dilute benzidine
ited in platinum. The iron bearing tungsten trioxide
usion with sodium carbonate, the melt extracted with
ron oxide filtered out and the solution acidified with h
using methyl orange). After addition of 10 cc. of sul
ungsten trioxide is precipitated with benzidine solution,
s before, ignited and weighed as trioxide. Watts (
nd Metallurgist, July, 1906; *Chem. News*, **95**, 19) dete
cid in natural and concentrated tungsten ores by tak
vith 50 cc. of hydrochloric and 15 cc. of nitric acid, bo
eating to near boiling for 4 hours in a covered beaker.
rated to 10 to 15 cc., 50 cc. of hot water and 5 cc. of h
dded. Tungsten trioxide is separated from silica by
ontaining some ammonium chloride. The ammonia
vaporated and the trioxide ignited and weighed.

Gold, Platinum Group, Tin.—Donau (*Monatsh.*, **27**,
new method for the determination of the metals, esp
alladium, through conductivity measurements. The
ut into a U conductivity measuring tube, reduced by c
nd the maximum effect of the carbon monoxide mea
rease of conductivity (d) is affected somewhat by ac
$0.000476 + 0.277l + 10l^2$ (l = initial conductivity). Ea
z mg. per 100 cc.) with definite initial conductivity ($
lifferent for the different amounts of hydrochloric acid
certain increase in conductivity ($x.10^{-4}$). The x y
nknown, an empirical function is assumed and an equa
he method of least squares. $z = 1.76\,x - 0.0237xy$
$0.0011\,x^2y + 0.000738\,xy^2$. The gold content can also b
graphic representation. The palladium determination
onductivity is only insignificantly affected by the fr
nd is nearly proportional within certain limits to the pa
The number of mg. of palladium per 100 cc. is given by mu
10^{-4} by the increase in conductivity. The mean error he
Maxson (*Am. J. Sci.* [4] **21**, 270; *Z. anorg. Chem.*, **49**,
actory colorimetric determinations of gold in small am
his red colloidal solution by mixing gold chloride and sa
cetylene solutions. The content of such solutions
gravimetrically and different concentrations were pre
dilution. First a Gallenkampf then a Penfield colori
The least determinable quantity was 0.000,01 gram; th
was 0.0008 with an error of 0.000,06. Petersen (*Z.*
342) instead of the usual separation of gold, platinum
arsenic in the hydrogen sulphide group, precipitated a
the group and some cobalt and nickel from weakly ac
zinc turnings. After warming for ½ hour the precipit
and warmed with dilute hydrochloric acid; cadmium, t
balt dissolved. The residue was washed, then boiled w

acid; mercury, lead, bismuth, copper, nickel dissolved leaving gold, platinum, antimony and some antimonic acid. This residue was ignited with 1 to 2 parts of ammonium nitrate and 5 parts of ammonium chloride in porcelain; antimony volatilized as chloride. The residual gold and platinum were dissolved in aqua regia, and detected through concentrated ammonium chloride or sulphur dioxide or alkaline hydrogen peroxide. Arsenic, antimony and zinc must be tested for in special portions. The original solution was tested for zinc by precipitating with sodium carbonate, dissolving the precipitate in hydrochloric acid, passing in hydrogen sulphide and decomposing with excess of sodium acetate; white zinc sulphide was precipitated. Orloff (*Chem.-Ztg.*, **30**, 714) observed that hydrogen peroxide seems to dissolve osmium and osmium hydroxide to a marked degree to osmium tetroxide. Histological specimens blackened by osmic acid are completely decolorized by hydrogen peroxide. From mixtures of the platinum metals obtained by reduction with zinc or magnesium the peroxide dissolves only osmium. Silver iodide rapidly blackens with palladium chloride or bromide, forming a mixture of palladium iodide and silver chloride. Soluble alkali and alkaline earth iodides form insoluble precipitates with salts of other platinum metals, hence a potassium iodide solution may be used only with certain precautions to separate palladium from the others. But freshly precipitated silver iodide changes only palladium chloride to black iodide. Thompson and Miller (THIS JOURNAL, **28**, 1115) determined melting points, cooling curves, microstructure, densities and electrical conductivities of platinum silver alloys containing about 10, 20, 30, 40, and 50 per cent. platinum. They concluded that it is not possible to separate platinum from gold, iridium, etc., by alloying with silver and dissolving in nitric acid, that platinum alloys of more than 20 per cent. platinum cannot be completely separated by concentrated sulphuric acid, and that the irregular results obtained from treating these alloys with nitric acid are caused apparently by the existence of platinum silver compounds. They analyzed the alloys by treating them hot with concentrated sulphuric acid in two portions, diluting, filtering and washing out the silver, then igniting the residue in porcelain. This residue was taken up in aqua regia and evaporated nearly to dryness with nitric acid. The solution was diluted and the silver precipitated with sodium chloride solution. The precipitate was washed free from chlorine, dissolved in ammonia and reprecipitated with nitric acid. From the solution in sulphuric acid the silver was precipitated after dilution either as sulphide or as chloride.

Reichard (*Pharm. Centrh.*, **47**, 391) gave a new reaction for tin, treating a little finely pulverized uric acid with some drops of stannic chloride solution, then adding concentrated sodium hydroxide to the mass dropwise with stirring till nearly all is dissolved and heating. A gray to intense black fleck is formed. Stannous compounds do not give the reaction, neither do arsenic or antimonic acid. Lead and cadmium do not give it. Copper hydroxide gives a black on heating without the uric acid, owing to the formation of copper oxide. Mercuric chloride gives a reddish brown compound. Bismuth gives the same reaction as tin but the precipitate is insoluble in sodium hydroxide. 0.0001 gram of tin may be detected. Nitric and hydrochloric acids destroy

the black residue only slowly and incompletely, sulphuric acid immediately.

Miscellaneous.—Rimini (*Atti accad. Lincei* [5] **15**, II, 320) stated that both Riegler and Ebler have overlooked his work on hydrazine volumetric methods. He modified his iodometric method by carrying out the determination in alkaline solution, thus avoiding the separation of iodine. $3N_2H_4.H_2SO_4 + 2KIO_3 + 6KOH = 3N_2 + 2KI + 3K_2SO_4 + 12H_2O$. Instead of Ebler's mercury method he proposed to add to a concentrated solution of hydrazine sulphate after neutralizing, using methyl orange as indicator, a certain excess of half-normal sodium hydroxide, then the mercury salt solution and then to heat. The solution was brought to definite volume and the excess of sodium hydroxide determined in an aliquot portion or in the filtrate with half-normal acid. $N_2H_4.H_2SO_4 + 2HgCl_2 + 5NaOH = 4NaCl + NaHSO_4 + Hg_2 + N_2 + 5H_2O$. Pannani's method for potassium persulphate gives too high results. Rimini added to a neutral solution of persulphate a solution of hydrazine sulphate neutralized with caustic potash, then shook this up with titrated caustic potash and determined the excess of alkali after 5 minutes. $2K_2S_2O_8 + N_2H_4.H_2SO_4 + 5KOH = N_2 + 5K_2SO_4 + 5H_2O$.

Puschin (*J. russ. phys.-chem. Soc.*, **38**, 764) gave a quantitative separation of tin from manganese, ferrous iron and chromium by electrolysis. Bivalent iron and manganese may be separated like cobalt and nickel from tin (*Ibid.*, **37**, 828). Trivalent manganese and chromium may also be separated easily from tin. A satisfactory separation of ferric iron and tin was not obtained.

Analysis of Organic Compounds.

General, Hydrocarbons, Derivatives.—Alvarez (*Chem. News*, **94**, 297; *Ann. chim. anal. appl.*, **12**, 9) observed that hydrated sodium peroxide, the color reagent for polyphenols, gives characteristic colors with some other compounds when 0.2 to 0.3 gram of peroxide and 0.05 to 0.1 gram of substance are treated with 5 cc. of alcohol, then after 4 to 6 minutes with 15 cc. of water. Emodine gives an intense light red, changed to yellow with acetic acid; chrysarobin a wine color, yellow with acetic acid, 1, 2-dihydroxyanthraquinone blue-violet, yellow with acids (blowing on the blue-violet solution causes it to turn red at edges); alizarin violet, orange with acids; 1,2,4-trihydroxyanthraquinone intense red-violet in alcohol, cherry-red in water; chrysophanic acid cherry-red in alcohol, lighter red in water; rosolic acid intense purple; purpurin alizarin-red; anthragallol almost black dark blue; dihydroxyquinone brown in alcohol, red in water, and ellagic acid brown-black in alcohol, yellow in water. Graefe (*Chem. Rev. Fett.- u. Harz-Ind.*, **13**, 30) stated that carbon tetrachloride surpasses all other ordinary solvents in the power to dissolve paraffin, for example at 20° of a paraffin of melting point 53.5° 1 cc. of ethyl acetate, dissolves 1.1, of acetone 1.2, 96 per cent. alcohol 1.9, ether 83.4, petroleum ether 200, ligroin 244, chloroform 246, benzene 285 and carbon tetrachloride 317 mg. Carbon tetrachloride also gives good results in the fractional precipitation of different paraffins. Nicloux (*Compt. rend.*, **142**, 163; *Bull. soc. chim.* [3] **35**, 321) determined small amounts of chloroform in air or in blood or an aqueous liquid by heating 60 cc. of alcoholic chloroform solution with 10 cc. of 10 per cent. alcoholic caustic potash for 30 to 45 minutes. The reaction $CHCl_3$ +

$4KOH = 3KCl + KHCO_3 + H_2O$ is quantitative. Fifteen cc. of water are added after cooling, the solution is neutralized with sulphuric acid, using phenolphthalein, and titrated with silver solution and potassium chromate as indicator. The error is 1 to 2 per cent. To determine chloroform in air the air is drawn through 2 wash flasks containing 96 per cent. alcohol at the rate of 2 liters per hour. In blood the five-fold volume of 80 to 95 per cent. alcohol acidified with 0.25 gram of tartaric acid is added, then 10 cc. of 95 per cent. alcohol, ⅓ of the liquid is distilled off and the rest of the determination carried out as above.

Reichard (*Pharm. Centrh.*, **47**, 309) observed that phenanthrenquinone dissolved in concentrated excess of primary sodium sulphite solution and warmed gave on cooling a colorless crystal mass which on standing for some weeks about 2/3 liquefied again. At the same time there formed at the upper edge of the crystal mass a red to red-brown ring, changing soon to gray and finally increasing in volume till the whole mass was colored gray, while the liquid was colored clear green. Dupré (*The Analyst*, **31**, 213) determined moisture in a substance containing other volatile material by putting the substance in layers in a tube 1 cm. wide and 12 long between layers of fine sand and calcium carbide, connecting the tube with a nitrometer filled with saturated sodium chloride solution. On warming on a water bath acetylene was obtained. One cc. of acetylene corresponds to 0.001725 gram of water. The method can be used on a substance like cordite. Raikow and Ürkewitsch (*Chem.-Ztg.*, **30**, 295) observed that solid pulverized caustic potash gives a brown color with nitrotoluene and nitrobenzene, weaker with the latter. Pulverized caustic soda does not act at ordinary temperatures with nitrobenzene (distinction from caustic potash) but gives a yellow-brown color with nitrotoluene. The reaction is more delicate when gasoline is used as a solvent (1 cc. for 0.5 gram of caustic soda). In 1 cc. of gasoline solution, 0.0025 cc. of nitrotoluene can be detected. To detect toluene in benzene both are converted into nitro compounds and tested. An approximate quantitative determination can be made by comparing the brown color with that caused by known amounts of nitrotoluene in gasoline solution. Alkali hydroxides in this reaction are effective in the order of the atomic weight of their metals, lithium hydroxide weakest, then those of sodium, potassium and rubidium.

Alcohols, Phenols.—Blank and Finkenbeiner (*Ber.*, **39**, 1326) determined the methyl alcohol in formaldehyde solutions by putting 1 gram of the solution into 50 cc. of twice normal chromium trioxide and 20 cc. of 98 per cent. sulphuric acid, diluting after 12 hours to 1 liter, adding a little potassium iodide to 50 cc. of this solution and titrating back with tenth-normal thiosulphate. Methyl alcohol $= 32\ (a\text{-}b)100/48$ per cent., where $a = 0.8$ gram (the amount of oxygen used $- 0.016 \times$ number of cc. of thiosulphate used) and $b =$ the oxygen needed for the oxidation of the formaldehyde. The latter is calculated from the formula $\frac{32 \times \text{per cent. content}}{30 \times 100}$. Fendler and Mannich (*Arb. Pharm. Inst. Univ. Berlin* III, 1) determined methyl alcohol in spirits by carefully heating 10 cc. of the liquid to boiling in a 50 cc. flask provided with a doubly bent tube for condenser. 1 cc. is distilled off in 4 to 5 minutes, 4 cc. of 2 per cent. sulphuric acid added and then gradually 1 gram of

pulverized potassium permanganate with cooling and shaking. The mostly reddish liquid is filtered and heated for 20 to 30 seconds at weak boiling, cooled and 1 cc. of the colorless liquid mixed with 5 cc. of concentrated sulphuric acid, then with 2.5 cc. of a fresh solution of morphine hydrochloride (0.2 gram in 10 cc. of concentrated sulphuric acid). With 0.5 per cent. methyl alcohol the liquid becomes in 20 minutes intense violet or violet-red in color. Voisenet (*Bull. soc. chim.* [3] 33, 748) applied his recently discovered reaction of formaldehyde with nitrite containing egg albumen (*Ibid.* [3] **33**, 1198) to the detection of methyl alcohol. An amount of the alcohol corresponding to 1 cc. absolute is diluted to 50 cc. with water, 5 grams of potassium bichromate and 3 cc. of 20 per cent. (by weight) sulphuric acid are added, shaken, let stand for an hour at the ordinary temperature, then distilled so as to obtain 30 cc. in 1 hour. These 30 cc. contain all the acetaldehyde and are thrown away. The following 20 cc. must contain the methyl alcohol and are tested for it. Aldehydes with phenol character give a similar violet color which is, however, quite stable toward reducing agents; the formaldehyde color is not. Gascard (*J. pharm. chim.* [6] **24**, 97) determined the molecular weight of alcohols and phenols by heating the dried substance in a long-necked flask with 2 to 3 times the theoretical amount of benzoic acid anhydride for 24 hours in a water or oil bath, the flask being covered. In most cases boiling calcium chloride solution (cold saturated) will do for the bath. 10 to 20 cc. of ether are run into the flask, then 5 cc. of water and 2 drops of phenolphthalein and the liquid titrated with normal potash. Molecular weight $P = p + 1000 / (N-n)$, where p = weight of substance, N = number of cc. of caustic potash, n = number of cc. of caustic potash found in the blank determination with everything but the alcohol or phenol. In the case of a polyalcohol the result is to be multiplied by the number of alcohol groups present. Where the benzoic acid ester is difficultly soluble in ether, benzene or chloroform are used. $ROH + (C_6H_5CO_2)_2O = C_6H_5.COOR + C_6H_5.COOH$. The free benzoic acid is titrated. Klason and Carlson (*Ber.*, **39**, 738) determined organic hydrosulphides and thioacids by titration with iodine and with alkalies. $2RSH + I_2 = R_2S_2 + 2HI$. Only thiocyanic acid is indifferent to iodine. Aromatic hydrosulphides are strong enough acids to give neutral salts with alkalies in alcoholic solution and as a result they can be titrated with alkali and phenolphthalein in alcohol solution. With the aliphatic hydrosulphides the indication is not sharp and with thioglycolic acid it fails, even in alcoholic solution. Rosenthaler (*Arch. Pharm.*, **244**, 373) used Nessler's reagent as a test for hydroxyl groups and found that, except benzhydrol, octyl and cetyl alcohols, all compounds that he tried containing primary and secondary alcoholic hydroxyl groups, on boiling for 1 minute gave reduction. These three did on boiling for some hours with a return condenser. Compounds with tertiary alcoholic hydroxyl do not reduce Nessler's reagent. Of compounds with phenol character—phenol, salicylic acid, guaiacol, thymol, resorcinol, phloroglucinol, and orcinol give no reduction, xylenols and creosol an unimportant, hydroquinone, pyrocatechol and gallic acid an energetic reduction. The Sacchse liquid reduces, but not the Knapp solution. Nessler's reagent may be used to test amylene hydrate for fermenting amyl alcohols and citric acid for tartaric.

Carobbio (*Boll. chim. farm.*, **45**, 365) tested for resorcinol by letting 1 to 2 cc. of the suspected ether flow down the wall of the test tube onto 1 cc. of zinc chloride with enough ammonia to give a clear solution. With 0.01 to 0.001 gram of resorcinol the place of contact turns yellow, then green and after a few minutes blue. Traces require considerably longer. Alcoholic hydrochloric acid added carefully forms a weakly red layer between the ring and the ether, spreading through the latter on shaking. By this reaction, 0.01 part of resorcinol per 1000 can be recognized in a few minutes. Hydroquinone gives the yellow ring, changing soon to a brown-red. Pyrocatechol and adrenaline give a garnet-red ring. Desmoulière (*J. pharm. chim.* [6] **23**, 244, 281, 332) determined glycogen by finding the amount of glucose pre-existing in the organ in question and that formed by hydrolysis. Two portions of the organ are taken, one of 10, the other of 40 grams. The 10 gram portion is digested with 0.15 gram of pepsin in the presence of water and a little sulphuric acid for 6 hours at 48° to 50°. A little more sulphuric acid is added and the whole heated to 115°–120° in an autoclave for 1.5 hours. The cooled contents of the autoclave are heated with slight excess of mercuric nitrate, then dilute caustic soda added to neutral or weakly alkaline reaction, the whole diluted and filtered. 100 cc. of the filtrate are shaken with 4 or 5 grams of zinc dust to separate the mercury, filtered, 50 cc. of this treated with caustic soda till the zinc precipitated dissolves again, water added to 55 cc. and the glucose determined gravimetrically or by titration. In the calculation the volume of the precipitate obtained in the purification should be subtracted from the volume of the liquid, here 200 cc. The glucose pre-existing in the solution is determined in the 40 gram portion by extracting with water, the united extracts are purified with mercuric nitrate and caustic soda, the volume brought to 1000 cc., the filtrate treated with zinc dust and the determination carried out as above. Ottolenghi (*Atti. accad. Lincei*, [5] **15** I, 44) stated that the reaction of Neuberg and Rauchwerger for the detection of cholesterol (with rhamnose and concentrated sulphuric acid) is not characteristic of cholesterol but is given by phytosterol from many sources. Neuberg (*Z. physiol. Chem.*, **47**, 335) admitted this to be true. Windaus (*Chem.-Ztg.*, **30**, 1011) detected small amounts of cholesterol in the presence of phytosterol by the difficult solubility of cholesterol dibromide in a mixture of ether and acetic acid. 100 cc. of a 50 per cent. mixture dissolves only 0.6 gram, 40 cc. ether and 60 cc. acid only 0.25 gram of cholesterol dibromide. Addition of a little water lowers the solubility while much water causes the phytosterol dibromide to separate out in an oily form and to crystallize with more difficulty. Cholesterol dibromide may be obtained almost quantitatively by dissolving cholesterol in a little ether and adding a solution of bromine in acetic acid (5 grams in 100 cc.). The use of petroleum ether gives a cholesterol salt of different melting point.

Aldehydes, Ketones.—Meth (*Chem.-Ztg.*, **30**, 666) stated that one of Rimini's (*Ann. farmacol.*, **98**, 97) tests for formaldehyde, that of the red color with ferric chloride, phenylhydrazine hydrochloride and hydrochloric or sulphuric acid, occurs also with acrolein even though with different shade and less delicacy. Rimini's other test with phenylhydrazine hydrochloride, sodium nitroprusside and sodium hydroxide giv-

ing with formaldehyde a blue color gives nothing with acrolein. Schoorl (*Pharm. Weekblad*, **43**, 1155) criticized Blank and Finkenbeiner's (*Ber.* **39**, 1326; see under alcohols) method for the determination of formaldehyde. He added to 3 grams of the formaldehyde solution a mixture of 50 cc. of normal alkali and 50 cc. of neutral 3 per cent. hydrogen peroxide, warming on a water bath, cooling and adding phenolphthalein. Hence it must take 16 to 17 cc. of normal acid to neutralize. Hérissey (*J. pharm. chim.* [6] **23**, 60) determined small amounts of benzaldehyde by distilling 50 cc. from the liquid resulting from the splitting of the glucoside, treating this with 50 cc. of a solution of 1 cc. of freshly rectified phenylhydrazine and 0.5 gram of acetic acid in 98.5 cc. of water, heating for 20 to 30 minutes on a water bath, then after 12 hours' standing, collecting in a Gooch crucible, washing, drying and weighing the phenylhydrazone. This weight multiplied by 0.54081 gives the weight of benzaldehyde. Wallis (*Pharm. J.* [4] **22**, 162) determined chloralhydrate by dissolving in 10 cc. of alcohol, digesting for 3 hours on a water bath with 10 cc. of a volumetric sodium hydroxide solution, neutralizing with sulphuric acid and titrating with standard silver nitrate solution. $CCl_3.CH(OH)_2 + 5NaOH = 3NaCl + 2HCOONa + 3H_2O$.

Auld (*J. Chem. Ind.*, **25**, 100) determined acetone by adding to a hot 10 per cent. caustic potash solution of the weighed liquid dropwise a solution of 200 grams of bromine and 250 grams of potassium iodide in 1 liter of water, heating for 1/2 hour at 70°, and distilling off the bromoform. The distillate is then heated with 50 cc. of alcohol and enough caustic potash to make a 10 per cent. solution, using a return condenser till all bromoform is decomposed. $3CHBr_3 + 3KOH + C_2H_5OH = 3CO + C_2H_4 + 9KBr + 7H_2O$. The distillate is titrated with silver nitrate solution. To 58 parts of acetone, 240 parts of bromine correspond. Jolles (*Ber.*, **39**, 1306) determined acetone by the addition of a 3- to 4-fold excess of titrated primary sodium sulphite titrating back after 30 hours' standing with iodine solution. $CH_3.CO.CH_3 + NaHSO_3 = CH_3.C(OH)(SO_3Na).CH_3$.

Acids.—Carletti (*Boll. chim. farm.*, **45**, 449) observed that furfural gives colors with the aromatic amines, at any rate with aniline, only in the presence of organic acids, not with aniline salts of mineral acids nor after the addition of a mineral acid to aniline originally combined with an organic acid. Two solutions are prepared; (*a*) 5 grams of pure aniline are treated with 25 cc. of concentrated acetic acid and diluted to 100 cc. with water, and (*b*) 1 gram of freshly prepared furfural is made up to 100 cc. with 95 per cent. alcohol. 50 cc. of wine or vinegar are decolorized with animal charcoal, 25 cc. of 95 per cent. alcohol added, 10 cc. of this solution shaken with 5 drops of (*a*), then 5 of (*b*). With no mineral acid there is a distinct reddish color reaching a maximum after 30 minutes. But with 1/1000 of free hydrochloric, nitric or sulphuric acid the solution keeps its original weak green color. The reaction fails only with wines to which gypsum has been added. Guarnieri (*Staz. sper. agrar. Ital.*, **38**, 906) detected benzoic and salicylic acids in tomato preserves by diluting and acidifying the extract with sulphuric acid (1:3), extracting with 1/2 volume of a mixture of equal parts of ether and petroleum ether, repeating with ether, evaporating after the addition of a little weakly ammoniacal water, filtering, adding 2 to 3

grams of freshly ignited carbon, when the odor of benzoic acid is evident. The cooled test treated with a drop of 1 per cent. ferric chloride gives a reddish brown precipitate in the presence of benzoic acid. A violet color changing to blood-red on shaking shows salicylic and a brown color, green on shaking, tannic acid. In the latter case the tannic acid is precipitated as iron tannate and salicylic acid detected in the filtrate by the violet color. The iron tannate is dissolved in hydrochloric acid, diluted and shaken with ether. On slow evaporation of the ether, crystals of benzoic acid appear and may be identified by the aniline blue reaction. Herzog (*Festschrift Adolf Lieben*, 440; *Ann.* **351**, 263) gave a test for lactic acid, treating the silver salt with iodine. $2R.CHOH.COOAg + I_2 = R.CHOH.COOH + RCHO + CO_2 + 2AgI$. The acetaldehyde may be detected with sodium nitroprusside and piperidine. Amino acids were carefully converted in the cold into the α-oxyacids by means of silver nitrite and their silver salts treated as above with iodine. Glycocoll, alanine and other higher homologues can thus be detected. Schloss (*Beitr. chem. Physiol. u. Pathol.*, **8**, 445) detected glyoxylic acid by means of indole and skatole. With no ring formed at contact zone between solution and skatole (0.2 gram in 100 cc.) there is no glyoxylic acid present. If a red or brown ring is formed, the following test should be tried. 20 cc. of liquid are decolorized with animal charcoal, 1 or 2 cc. of dilute sulphuric acid added to a portion of the colorless filtrate and let stand for 10 minutes in a water bath at 50°. The skatole reaction should be set up in another portion, adding about 1 cc. of skatole solution and pouring concentrated sulphuric acid down to the bottom. The first portion is tested with indole. A sharp red ring after at most 2 or 3 minutes points to the presence of glyoxylic acid. The skatole reaction alone is not positive. Glyoxylic acid to 0.000,01 gram can be thus detected in wine. Sullivan and Crampton (*Am. Chem. J.*, **36**, 419) detected tartaric acid or tartrates by means of the crystalline structure of the calcium salt. 50 cc. of the concentrated salt solution containing not more than 30 per cent. of dry substance are rendered alkaline with caustic potash, a few drops of 20 per cent. potassium acetate added, acetic acid to acidification and then 10 cc. of 30 to 40 per cent. calcium chloride solution. The mixture is stirred for 1 to 2 minutes and allowed to stand for 12 to 15 hours at room temperature. The calcium tartrate crystallizes in rhombic prisms or pyramids recognizable under the microscope. No other organic acid gives a calcium salt of similar form. Citric and oxalic acid precipitate, malic does not, but in the presence of these acids the calcium tartrate is thrown out in needles and plates. Tocher (*Pharm. J.* [4] **23**, 87) used a couple of reactions for the detection of citric, tartaric and malic acids. Tartaric on heating with concentrated sulphuric acid gives a black mass, citric a yellow solution and malic a dark solution. Tartaric gives with cobalt nitrate a red solution becoming colorless with excess of caustic soda, deep blue on boiling, the color fading out on cooling. Citric gives a deep blue solution, and a precipitate if the neutral solution be boiled with calcium chloride solution. Malic gives also a blue solution but no precipitate with calcium chloride and gives on heating with dilute sulphuric acid and potassium bichromate the odor of ripe fruit. Ulpiani and Parrozzani (*Atti accad. Lincei*, [5] **15** II, 517) gave a rapid determination of citric acid in lemon juices, determining

first the approximate total acidity of the juice with normal sodium hydroxide, then putting 50 cc. in a 200 cc. flask with enough normal sodium hydroxide to neutralize about 1/10 of the total acidity. This value represents the maximum proportion of tartaric and oxalic acids which are then precipitated after the addition of about 17 grams of calcium chloride and 5 grams of animal charcoal and boiling. The mixture is cooled, made up to volume and filtered. The following determinations are made in the filtrate: (1) 50 cc. are titrated with normal sodium hydroxide till a faint permanent turbidity appears, and (2) another 50 cc. are boiled and titrated with the caustic soda to turbidity. The difference in sodium hydroxide between (1) and (2) represents 2/3 of the free and combined citric acid in the juice. Kastle (*Public Health and Marine Hospital Service U. S. Hygienic Lab. Bull.*, No. 26, 31) stated that small amounts of saccharin heated with small amounts of a reagent (5 cc. of phenol and 3 cc. of concentrated sulphuric acid) for 5 minutes at 160° to 170°, the mass dissolved in a little water and made alkaline with twice normal caustic soda, gives a purple or deep red color according to the amount of saccharin. The limit is 0.025 mg. Salicylic and benzoic acids do not interfere, neither do cumarin or ethyl *p*-sulphobenzoate. Vanillin becomes yellow, then red in the cold; heated to 160° to 170° it is first blood-red, then almost black; after the addition of caustic soda it is deep dark red. With other phenols substituted for ordinary phenol in the test the following colors are obtained:

Phenol	Saccharin at 160° to 170°	Vanillin at 100°
Pyrocatechol	Green	Dark blue to green
Hydroquinone	Dark red-brown with blue fluorescence	Dark red-brown
Resorcinol	Salmon color with strong green-yellow fluorescence	Red with weak green fluorescence
Tricresol	Purple-red	Deep purple-red
Phloroglucinol	Wine-red	Yellow
Thymol	Clear blue	Clear red

Cumarin at 100° gives colorless (with tricresol) to orange-yellow (with phloroglucinol) compounds. Stanek (*Z. physiol. Chem.*, **47**, 83, 334; *Z. Zuckerind. Böhmen*, **31**, 316) found that choline precipitates from acid or alkaline solutions with potassium triiodide while betaine precipitates only from acid. To 25 cc. of at most a 5 per cent. solution of the mixture of both hydrochlorides 5 per cent. primary potassium or sodium carbonate is added and precipitation made with the triiodide; the choline periodide is filtered, washed and the nitrogen determined. The filtrate is concentrated to about 25 cc., then about 10 per cent. sulphuric acid added, the liquid saturated with sodium chloride, and potassium triiodide added as long as a precipitate forms. This is filtered, washed with saturated sodium chloride solution and the nitrogen determined. The action of other nitrogen bases with potassium triiodide is tabulated and the method applied to the determination of choline and betaine in vegetable substances.

Derivatives of Carbonic and Uric Acids, Heterocyclic Compounds.—Ackermann (*Z. physiol. Chem.*, **47**, 366) recommended benzene sulpho-

guanidine as a means of detecting guanidine in the presence of arginine. 3 grams of guanidine carbonate warmed in 30 cc. of water are shaken with 6 cc. of 33 per cent. caustic soda and 4 cc. of benzene sulpho-chloride when, on cooling, white crystals of benzene sulphoguanidine separate out. They may be recrystallized from boiling water and boiling alcohol, and melt at 212°. In 100 cc. of water 0.02 gram is soluble. Arginine does not give the corresponding compound. Cumming and Masson (*Chem. News*, **93**, 5, 17. From *Proc. Soc. Chem. Ind. Vierona*, 1903, July–August) gave a new method for the determination of cyanates in the presence of carbonates. $KCNO + 2HCl + H_2O = KCl + NH_4Cl + CO_2$. The titration is first made in the cold for carbonates, with congo red or methyl orange as indicator, then an excess of acid is added, the solution boiled and the acid excess titrated back. A second determination of the cyanic acid may be made by boiling the solution containing the above reaction products with excess of caustic potash and determining by titration the amount of the latter required to break up the ammonium chloride. Herter and Foster (*J. Biol. Chem.*, **1**, 257; **2**, 267) gave an indole determination, treating a dilute solution (1:100,000 of water) made weakly alkaline with caustic potash with a drop of 2 per cent. β-naphthoquinone sodium monosulphonate, yielding a blue or blue-green color. With more indole, well formed crystals of a bluish color are obtained. The green color fails at a dilution of 1:1,024,000. The compound is soluble in chloroform with red color and this solution may be used for colorimetric work. Skatole is separated from indole by distillation and determined by a colorimetric method which rests on the blue color caused by Ehrlich's reagent. Konto (*Z. physiol. Chem.*, **47**, 185) detected indole in putrid albumen by distilling off 1/3 of an alcoholic solution, making the distillate alkaline with caustic soda and distilling, making this distillate acid with sulphuric and distilling. To 1 cc. of this are added 3 drops of 4 per cent. formaldehyde and an equal volume of concentrated sulphuric acid allowed to flow onto it. With a trace of indole the whole solution becomes a magnificent violet-red. The reaction is visible with 1 part of indole in 700,000 of water, but not in 800,000. Ronchèse (*J. pharm. chim.* [6] **23**, 336) determined uric acid with titrated iodine, 100 cc. of urine being treated with 15 cc. of ammonia and 15 grams of ammonium chloride, the precipitate filtered and washed with a solution of 150 cc. of ammonia and 150 grams of ammonium chloride per liter, brought into solution in 300 cc. of water with some acetic acid, 20 cc. of saturated borax and primary potassium carbonate solution are added and the solution titrated. The number of grams of uric acid in 1 liter of urine is equal to the number of cc. of tenth-normal iodine multiplied by 0.084 plus 0.01. 1 molecule of uric acid requires 2 atoms of iodine. Sperling (*Z. Oesterr. Apoth. Ver.*, **44**, 51) treated 2 to 3 cc. of a 1:100 aqueous solution of phenyldimethylpyrazolone with 2 drops of fuming nitric acid and after the appearance of the green color, added carefully 5 cc. of concentrated sulphuric acid. A cherry-red ring was obtained at the contact zone, which spread through the whole liquid on shaking. The reaction is characteristic for antipyrine and its derivatives except amidopyrine. Other substances treated as above gave the following results:

	2 cc. of solution of strength.	Addition of nitric acid caused.	Addition of sulphuric acid gave.
Salicylic acid	1:500	.....	gold-yellow color
Quinine sulphate	1:100	.....	" " "
" hydrochloride	1:200	.....	" " "
Cocaine "	1:100	.....	colorless
Codeine "	1:100	.....	orange-yellow
Phenol	1:100	wine-yellow color	red-brown and clouding
Resorcinol	1:100	yellow-brown color	vigorous gas evolution
Antipyrine salicylate	1:200	green color	cherry-red zone
Migranine	1:100	" "	" " "
Tussol	1:100	" "	" " "
Pyramidone	1:100	violet "	wine-yellow color

Weehuizen (*Pharm. Weekblad*, **43**, 1105) gave a number of microscopic reactions for pyramidone in 1:100 solution, with iodine-potassium iodide, bromine-potassium bromide, potassium cadmium iodide, mercuric chloride and sodium palladous chloride and in strength 1:400 with Mayer's solution. The precipitates are all crystalline and are characteristic.

Albumens.—Arny and Pratt (*Am. J. Pharm.*, **78**, 121) determined casein in milk by adding to 10 cc., 20 cc. of tenth-normal iron alum solution (48.1 grams per liter) in the cold, filtering, washing, acidifying with hydrochloric acid, adding potassium iodide and titrating the filtrate with tenth-normal sodium thiosulphate. Bordas and Touplain (*Compt. rend.*, **142**, 1345) made use of the insolubility of the chief albumens like egg, fibrin and casein and of gelatinous substances like diastases and peptones in pure or suitably diluted aqueous acetone for their determination. The mass must be neutral or at most only slightly alkaline or acid. 10 grams of butter, for instance, were treated with pure acetone, the residue washed with aqueous acetone, the residue containing the casein and ash. Levene and Rouiller (*J. Biol. Chem.*, **2**, 481) determined tryptophane in the products of hydrolysis of egg albumen. The liquid to be tested is made to contain 5 per cent. sulphuric acid and treated gradually with Hopkins and Cole's reagent (10 parts of mercuric sulphate and 90 of 5 per cent. sulphuric acid). Bromine water is added till the red color of the liquid over the precipitate begins to disappear. The liquid is filtered after 24 hours and the mercury precipitated with hydrogen sulphide. The filtrate is heated, made up to a definite volume, 15 cc. of this are treated with 2 cc. of amyl alcohol and then bromine solution added with vigorous shaking till the purple color of the alcohol solution disappears. In the presence of tyrosine the mercury precipitate with the reagent is treated with 5 per cent. sulphuric acid till the tyrosine reaction disappears. In the presence of cystine (1) the cystine-tryptophane solution is titrated with bromine, (2) an acid determination is made in an aliquot portion of the solution, (3) the amount of bromine corresponding to cystine is calculated and subtracted from the value in (1). The bromine solution is standardized against tryptophane and cystine solutions.

Carbohydrates.—Bang (*Biochem. Z.*, **2**, 271) determined sugar after its reduction of a copper solution by titration of the copper oxide remaining with hydroxylamine solution. The copper solution was made by dissolving 250 grams of potassium carbonate, 200 of potassium thiocyanate and 50 of primary potassium carbonate in about 600 cc. of water

at 50° to 60°, cooling to 30° and allowing 12.5 grams of purified copper sulphate pentahydrate dissolved in about 75 cc. of water to flow in, filtering after 24 hours and diluting to 1 liter. The hydroxylamine solution contained 6.55 grams of the sulphate and 200 grams of potassium thiocyanate dissolved and made up to 2 liters with water. 10 cc. of the sugar solution were boiled quietly for 3 minutes with 50 cc. of the copper solution, cooled quickly and titrated to colorless. The limit of the method lies at about 0.1 mg. of sugar. The copper reduced by the sugar precipitates as cuprous thiocyanate and the rest of the copper does also after reduction by the hydroxylamine. Browne (THIS JOURNAL, **28**, 439) analyzed sugar mixtures by determining the total content of reducing sugar as glucose and the polarization. If x = per cent. of sugar A, y of B and a the relation of reduction capacity of sugar A to that of glucose, b that of sugar B to that of glucose and R the per cent. of reducing sugar as glucose $ax + by = R$ and $\alpha x + \beta y = P$, α and β being the polarization factors of A and B respectively and P the polarimeter value. $x = \frac{bP - \beta R}{ab - a\beta}$ and $y = \frac{R - ax}{b}$. With these formulas the author has determined amounts of common reducing sugars like glucose, fructose, galactose, xylose and arabinose. The reduction constants of these sugars toward glucose were determined experimentally to be for fructose 0.915, galactose 0.898, xylose 0.983 and arabinose 1.032. Chavassier and Morel (*Compt. rend.*, **143**, 966) stated that 10 cc. of a reagent (1 gram of *m*-dinitrobenzene dissolved in 100 cc. of alcohol and 35 cc. of 33 per cent. caustic soda added) with 20 cc. of 1 per cent. aqueous sugar solution gives with maltose, lactose, galactose, glucose or arabinose inside of 15 minutes, with levulose inside 2 to 3 minutes, a violet color, while solutions of saccharose and glycogen are not changed. Aldehydes and ketones without the alcohol group give a red color which can cover the violet. Uric acid gives the same color as reducing sugars. Glassmann (*Ber.*, **39**, 503) gave two indirect volumetric methods for the determination of grape sugar. In one the sugar solution is added to a boiling excess of the Liebig-Knapp solution (alkaline mercuric cyanide) or to Sachsse's solution (alkaline potassium mercuric iodide). The precipitated mercury is filtered off and dissolved in concentrated nitric acid. This solution is diluted, treated with 1 to 2 cc. of saturated iron alum solution and the amount of 30 per cent. nitric acid necessary for complete decolorization, then the solution is titrated with hundredth-normal ammonium thiocyanate. (*a*) $CH_2OH.(CHOH)_4.COOH + 3Hg(CN)_2 6KOH = COOH.(CHOH)_4.COOH + 4H_2O + 6KCN + 3Hg$ (*b*) $CH_2OH.(CHOH)_4.COOH + 3K_2HgI_4 + 6KOH = COOH.(CHOH)_4.COOH + 4H_2O + 12KI + 3Hg$. One cc. of the thiocyanate solution corresponds to 0.001,001,5 gram of mercury. In the other method the grape sugar solution is boiled 10 minutes with a measured excess of alkaline mercuric cyanide, filtered from the mercury, the filtrate put into a Hempel nitrometer and the nitrogen evolved on the addition of hydrazine sulphate measured (Ebler, *Z. anorg. Chem.*, **47**, 377). The difference between the amount of mercury taken and the amount corresponding to the nitrogen gives the amount precipitated by the grape sugar. Arnold (*Ber.*, **39**, 1227) observed that these methods of Glassmann cannot be used with urines containing

creatinine, for this substance reduces alkaline mercuric cyanide in the cold and alkaline potassium mercuric iodide on warming. Lewinsky (*Berl. klin Wochschr.*, **43**, 125) showed that such substances as peptone, Liebig's beef extract, hydrolyzed casein, gelatin and glycogen in solution concealed the presence of varying amounts of glucose and glucoseamines. For instance in a solution containing 2 per cent. peptone 0.5 per cent. sugar gave no reduction with Fehling's solution and 1 per cent. gelatin concealed 0.005 per cent. sugar. Grape sugar can be approximately determined in fruit according to Lyon (THIS JOURNAL, **28**, 998) by obtaining the amount of soluble substances and the inversion polarization. The former is obtained from the density of the solution. If a = per cent. of soluble substance, b = polarization, x = per cent. of glucose, y = per cent. of cane and invert sugar then $x + y = a$ and $1.75x - 0.34y = b$ or $x = (0.34a - b)/2.09$. Both numbers in the formula change a unit in the second decimal for a change of 2° in temperature. Pellet (*Bull. assoc. chim. sucr. dist.*, **23**, 1015) observed that alcoholic digestion is of no value in sugar beet investigations and that errors come even from filtering in the alcoholic extraction. Cellulose (of the paper) absorbs sugar in alcohol solution and in the alcoholic digestion the cell substance may absorb oxygen, as has been observed by Hoglund and Crocker respectively. An absorption of sugar by cellulose does not take place in aqueous solution. Schoorl and Van Kalmthout (*Ber.*, **39**, 280) gave some color reactions of the most important sugars, criticizing some of Pinoff's (*Ibid.*, **38**, 3308). Ten cc. of an alcohol-sulphuric acid mixture (750:200), 0.05 gram of sugar and 0.2 cc. of 5 per cent. alcoholic α-naphthol solution give a red-violet in 1 minute if fructose or cane sugar were used, with *d*-glucose or milk sugar after 15 minutes (instead of 30). If the sugar solution be diluted with 10 cc. of alcohol, the color comes in 5 minutes with the first two sugars and with last two within 1/2 hour (instead of not at all). The β-naphthol reaction is given by Pinoff as characteristic for fructose but after 20 minutes fructose gives only a slightly darker yellow color than cane sugar, while after 30 minutes both glucose and milk sugar give a weak yellow color. Pinoff's reaction with resorcinol is a not specially fortunate modification of the Selivanow test. With potassium bichromate and ammonium chloride Pinoff said only the ketoses (fructose) gave a precipitate, but within 1/2 hour cane sugar gives at least a small precipitate. The formation of calcium fructosate is the only certain test for fructose. Berg's reaction for the detection of aldoses in opposition to ketoses and nonreducing polyoses (oxidation of the aldose to hydroxy acid with bromine and yellow color of this with ferric chloride) is not reliable because other carbohydrates color ferric chloride yellow, even though weakly. Talon (*Ann. chim. anal. appl.*, **11**, 244) found that the esters of glucose are always formed in the presence of alcohol and traces of acid, that they increase in amount with the temperature and the time and that they have no reducing power. So alcohol, even methyl alcohol, is to be avoided in tests or determinations of sugars. Glycerol esterifies like a monatomic alcohol on glucose and fructose but its action at the same dilution is less. Weehuizen (*Pharm. Weekblad*, **43**, 1209) observed that glucose, milk and cane sugar, starch and cellulose give with skatole a beautiful stable violet color and with indole a brown-red, if warmed at

the same time with strong hydrochloric acid. The skatole reaction is delicate to 1 : 300,000.

Baur and Polenske (*Arb. kais. Gesundheitsamt*, **24**, 576) separated starch and glycogen by dissolving 0.1 mg. of the mixture in 30 cc. of water and treating with 11 grams of finely divided ammonium sulphate. The starch is filtered and washed with ammonium sulphite solution (11 grams per 30 cc.). Glycogen is precipitated out of the 60 cc. of filtrate on dilution with water to 500 cc. and addition of 500 cc. of alcohol. Jolles (*Ber.*, **39**, 96; *Monatsh.* **27**, 81; *Z. anal. Chem.*, **45**, 186) applied his titration with primary potassium sulphate to the determination of pentoses, changing them first to furfural by distilling with hydrochloric acid and steam, taking then an aliquot portion of the distillate, neutralizing, treating with a measured excess of sulphite and titrating back after 2 hours with iodine. $C_4H_3O.CHO + HKSO_3 = C_4H_3O.CHOH.SO_3K$. Pflüger (*Pflüger's Arch.*, **114**, 231) determined glycogen by warming 100 grams of the organ in question for 3 hours in a boiling water bath with 100 cc. of 60 per cent. caustic potash. After cooling, the solution is diluted to 400 cc. and precipitated with 96 per cent. alcohol. The glycogen precipitate is allowed to stand, then washed with alcohol and ether, then dissolved in hot water, the aqueous solution made up to a definite volume and the glycogen determined by polarization. It may be inverted and the sugar determined.

Alkaloids.—Georges and Gascard (*J. pharm. chim.* [6] **23**, 513) stated that the color of a neutral or weakly alkaline solution of morphine with iodic acid (yellow to reddish yellow and yellow-brown if made weakly alkaline with ammonia) may be used for the colorimetric determination of morphine. The iodic acid color is sharpest at dilutions from 1 : 500 to 1 : 5000; the iodic acid-ammonia color at dilutions greater than 1 : 2500. The first color reaches a maximum in 1/2 minute and remains unchanged for 15 minutes. The alkaline color is at a maximum after 2 to 3 minutes. Mai and Rath (*Arch. Pharm.*, **244**, 300) gave another colorimetric determination of morphine, using Marquis's reagent (2 drops of 40 per cent. formaldehyde and 3 cc. of sulphuric acid). One cc. of a 1 : 1000 solution of morphine is evaporated in glass on a water bath and the residue stirred with 1 cc. of the reagent, the deep violet colored solution put in little tubes of about 10 mm. width and after washing out the dish, diluted with 4 cc. of sulphuric acid. The limit of delicacy is about 0.000,03 gram of the alkaloid. Radulescu (*Bull. Soc. Sciinte Bucuresci*, **14**, 602) added to a clear solution containing 1 : 300,000 or more of morphine, a kernel of sodium nitrite and an acid, making the solution alkaline before the end of the gas evolution with concentrated aqueous caustic potash. The solution is pale red to deep ruby-red according to concentration. The color disappears on acidification, reappears on making alkaline and is not taken up in ether, chloroform, carbon bisulphide or benzene. On long standing or on boiling, the acid solution loses its property of becoming colored by alkalies. Herder (*Arch. Pharm.*, **244**, 120) observed that the ease of solubility of alkaloid precipitates in alkali and alkaline earth mercuric iodides decreases with rise of atomic weight of the metal and that differently from the precipitate in aqueous solutions which in 30 per cent. chloralh ydrate is almost always crystalline. The limits of sensibility of pure alkaloids toward caesium mercuric iodide in aqueous (I)

and in 3 per cent. chloral hydrate (II) solutions and toward barium m
curic iodide in aqueous (III) and in chloral hydrate (IV) solutions
given as follows:

	I.	II.	III.	IV.
Berberine	1:300,000	1:65,000	1:500,000	1:80,00
Hydrastine and canadine	1:30,000	1:2000	1:38,000	1:2400
Strychnine	1:200,000	1:40,000	1:220,000	1:43,00
Brucine	1:40,000	1:10,000	1:41,000	1:11,00
Quinine	1:100,000	1:20,000	1:10,000	1:25,00
Cinchonine	1:90,000	1:10,000	1:100,000	1:12,00
Coniine	1:1300	below 1:1000	1:1300	below 1:1000

The alkaloids were detected and localized in sections of a numbe
plants. Coniine gives no precipitate in aqueous solution. The se
treated with barium mercuric iodide solution is washed quickly with w
and laid in a 0.5 per cent. solution of potassium bichromate in 30
cent. chloral hydrate and acidified with a few drops of hydrochloric
A yellow to yellow-brown solution indicates the alkaloid. Jonescu
pharm. Ges., **16**, 130) observed that by Thoms's method of pr
itation with potassium bismuth iodide and decomposition of the
cipitate with alkali not only atropine and hydroscyamine but qui
caffeine and antipyrine may be nearly quantitatively precipitated.
1 gram of quinine used the author obtained 0.9405 gram, of caf
0.9546 and of antipyrine 0.9273 gram. Monti (*Gaz. chim. ital.*, **36**
477) criticized the reaction of Alvarez for aconitine and gave one o
own. The alkaloid (0.0002 to 0.001 gram) was treated in porc
with 2 to 4 drops of sulphuric acid (d. 1.75 to 1.76) heated for 5 or 6
utes on a boiling water bath, then a small amount of resorcinol a
and the whole warmed further. A yellow-red color appears, atta
a maximum after 20 minutes. Thus 0.0001 gram can be detected. R
ard (*Chem.-Ztg.*, **30**, 109 on picrotoxine; *Pharm. Ztg.*, **51**, 168, 591 o
caine, 532 on quinoidine, 817 on opium alkaloids; *Pharm. Ce*
47, 247 on morphine, 347 on cocaine, 473 on berberine, 623 on theb
727 on codeine, 1028, 1048 on narceine) has again published a s
of articles on alkaloids.

Coloring Materials, Oils.—Green, Yeoman and Jones (*Mon.*
[4] 20 I, 181) gave a method for the systematic analysis of colors on
mal fibers. The method includes two operations; in the first the
is removed from the fiber and its chemical behavior studied, in the
ond it is reduced and the course of its reoxidation studied. Given
coloring matter alone it is reduced with zinc dust and oxidized
air and with chromium trioxide; if on the fiber it is reduced with hy
sulphite and oxidized with air and potassium persulphate. Their cl
fication follows: I. Decolorized by hydrosulphite and regener
in air: azines, oxazines, thiazines, indigo. II. Decolorized by hy
sulphite, not regenerated in air but by chromium trioxide: triphe
methane colors. III. Destroyed by hydrosulphite: nitroso and n
azo colors. IV. Not changed by hydrosulphite: pyrones, acrid
quinoleins, thiazoles, certain anthracene colors. V. Changed to br
products by hydrosulphite and regenerated in air or by potassium
sulphate: most anthracene colors. Knowing the class, chemical
tions and shade the choice is limited to a few closely allied colors. Gr

(*Chem.-Ztg.*, **30**, 298, 299) gave the following main differences between lignite pitch and other pitches.

	Melting point.	Residue after extraction with benzene.	Sulphur.	Iodine value.
Lignite pitch	86°	0.0	2.14	93.7
Coal tar pitch	91–92°	46.0	0.31	50.0
Wool fat pitch	32°	0.0	0.00	36.9
Stearin pitch	43°	0.0	0.67	40.4
Petroleum pitch I	33°	2.0	1.17	49.4
Petroleum pitch II	73°	3.5	1.09	70.3
Petroleum pitch III	126°	4.0	1.00	103.5
Lignite "goudron"	52°	0.0	1.88	66.5
Wood pitch	195°	42.0	0.00	140.0

A test for phenols which serves to distinguish lignite pitch from other pitches is given. A little of the asphalt is pulverized and boiled with some normal caustic soda and filtered. A little of a solution of a few drops of aniline in 1 cc. of hydrochloric acid and 10 of water with some sodium nitrite solution added in the cold is added to this alkaline liquid. A red or reddish brown color or precipitate appears according to the phenol content. Without phenols the liquid is only yellow. Valenta (*Ibid.*, **30**, 266) used methyl sulphate in the detection and determination of tar oils. It dissolves the hydrocarbons of the benzene series or mixes with them in all proportions while hydrocarbons with open carbon chain and petroleum distillates do not dissolve in the cold and even esters are difficultly soluble. A measured amount of the oil sample is poured into a 100 cc. glass stoppered measuring cylinder and 1.5 to 2 times as much methyl sulphate added. The whole is shaken and the volume of the lower liquid after separation read, the difference giving the amount of oil dissolved. The tar oils may be precipitated from solution by caustic potash. A gravimetric determination is possible if the caustic soda be neutralized, the whole shaken with alcohol and the oil weighed after driving off the latter. Rebs (*Protokoll 1. Stzg. Komm. Bekämpf. Missverständ., Herst, etc., Farben u. Malmaterialien Nürnberg*, **1906**, 35) determined turpentine resins or abietic acid in resins of various sorts, oil and copal lacs, pitch and paper by treating 10 grams of substance with 20 to 25 cc. of 10 per cent. alcoholic potash, warming, decomposing the soap, after cooling, with dilute hydrochloric acid and filtering, washing and drying the separated resin. The pulverized resin is extracted with 50 cc. of warm petroleum ether, the abietic acid precipitated from the filtered solution as ammonium salt, separated and the ammonia driven off by gentle heat. The remaining resin-like mass gives the resin content of the substance. For less accurate work the substance may be extracted with benzene and the saponification omitted. Vaubel (*Z. öffentl. Chem.*, **12**, 107) simplified his last year's method for determining turpentine oil in the commercial product by adding to 1 to 2 grams of oil in chloroform 100 cc. of water, 5 grams of potassium bromide and 10 cc. of concentrated hydrochloric acid or a corresponding amount of sulphuric acid and then titrated potassium bromate solution till a permanent bromine color appeared. Genuine oils of turpentine have a bromine absorption of 220 to 230 while that of substitutes falls as low as 16 sometimes. Paulmyer (*La Savonnerie Marseillaise*, **6**, No. 62;

Seifensiederztg. **33**, 286) made use of the "critical solution temp ture" of various fatty oils for detecting adulterations in cocoanut A cloudy mixture of fatty acids warmed with acetic acid will clear suddenly and the temperature at which it does so is constant for e acid (critical solution temperature). With pure cocoanut oil fatty a the liquid clears at 33°. Warmed a little above this and allowed to with stirring it will cloud at 33°. The value for various acids is:

Cocoanut oil.....	33°	Rape oil.....	107°	"Palmkernöl"..	49°
Earthnut oil.....	90°	Linseed oil....	72°	Stearic acid....	94° (commerci
Sesamé oil.....	89°	Olive oil.....	93°	Oleic acid.....	98° "
Niger oil.....	85°	Cotton oil.....	82.5°		
Castor oil	13.5°	"Mafentalg"..	88°		

With mixtures of the fatty acids the difference in solubility temp tures is proportional to the quantities of single acids present. Twit (THIS JOURNAL, **28**, 196) found that a fat with excess of water and than 1 per cent. of naphthalenestearosulphonic acid will be almost c pletely saponified in 8 to 10 hours. This acid tried on a soluble gly ide, triacetin, showed about the same hydrolyzing power as hydroch acid, but the latter has practically no action on an insoluble glyce like a common fat while the organic acid works almost as well as soluble ester. The capacity of these sulpho fatty acids to dissolv well in fatty acids as in water and to make fatty acids soluble is of v in the separation of solid and liquid fatty acids.

Butter, Milk.—Robin (*Compt. rend.*, **143**, 512) detected cocoa fat margarine in butter by means of the facts that the fatty acids of c fat are nearly completely soluble in 56.5 per cent. alcohol at 15° those of butter are only partly and those of margarine difficultly sol and that the content of water-soluble fat in butter is much larger in the others. The butter sample is heated with alcoholic ca potash and the liquid so diluted with water after cooling that a 56.5 cent. alcohol results. A blank determination with the same am of alcoholic caustic potash is carried out, and both are titrated half-normal hydrochloric acid in 56.5 per cent. alcohol. The differ gives the amount of acid needed for the separation of the fatty in the first flask and the soap there is decomposed with this amou acid, the liquid diluted to 150 cc. with 56.5 per cent. alcohol, cool 15° and filtered. In 50 cc. of the filtrate is found by titration with t normal caustic potash the amout of fatty acids soluble in 56.5 per alcohol. Another 50 cc. are evaporated to 15 cc., the water-inso fatty acids filtered out, dissolved in a mixture of alcohol and ethe trated, thus giving the amount of fatty acids soluble in 56.5 per alcohol but insoluble in water. The difference between these two ues gives water-soluble acids.

	Butter.	Margarine.	Coco
Acids soluble in alcohol.....	11.67–14.83	2.67	46
" insoluble in water.....	5.51– 8.31	2.56	44
" soluble " "	5.92– 6.66	0.11	1
Water insoluble: water soluble.	8.3 –12.7	231.7	225

Alcock (*Pharm. J.* [4] **23**, 28) detected formaldehyde in milk by ing to 2 cc. the same volume of 20 per cent. caustic potash, shaking hen adding an excess of strong hydrochloric acid and warming caref

A coagulum is obtained, colored more or less deep violet according to the amount of formaldehyde, while the liquid below remains colorless. Bonnema (*Pharm. Weekblad*, **43**, 434) found that the mean freezing point of milk is $-0.555°$ and that it is influencd by dissolved crystallizable substances. The amount of water added can be determined by means of the change in freezing point. $D = \frac{0.555 \times 88.5}{w + 88.5}$ or $w = \frac{0.555 \times 88.5}{D} - 88.5$, where w is the weight of water added in grams and D is the freezing point in degrees below zero. This formula applies to milk with an average of 88.5 per cent. water. The freezing point rises a few hours after milking because of the formation of ammonia by bacteria and by which some phosphates are precipitated. The subsequent lowering is due to the formation of lactic acid which dissolves some of the precipitated phosphates. Comanducci (*Rend. accad. scienze fisiche e matem. Napoli*, **1906**, April) observed that a certain amount of pure milk requires always the same amount of potassium permanganate to oxidize the organic matter in it. Watering can be detected in this way. 1 cc. of cow's milk requires 50 to 52 cc. of tenth-normal permanganate, goat's milk 44 to 46, sheep's 43 to 48, ass's 55 to 58, woman's 53 to 60, these oxidation indices sinking if the milk is adulterated. Cow's milk with 10 per cent. of water requires 44 cc. permanganate for 1 cc., 20 per cent. 39. With half the cream removed the oxidation index fell also to 44 to 46. Cow's milk with an oxidation index of less than 50 is therefore suspicious. Lelli (*Arch. farmacol.*, **5**, 645) detected primary sodium carbonate in milk by means of aspirin. Milk, an equal volume of water and a little aspirin are heated to 60°, the opaque solution filtered, and the filtrate treated with a little 10 per cent. ferric chloride solution. In presence of the carbonate an abundant red-yellow precipitate is formed. 0.5 per cent. of carbonate can be detected. Trillat and Sauton (*Compt. rend.*, **142**, 794; **143**, 6; *Bull. soc. chim.* [3] **35**, 906, 1207) gave a determination of the albuminous substances of milk and the casein of cheese, making use of the property of formaldehyde of rendering these albuminoids insoluble without changing their weight. 5 cc. of milk are diluted with 20 cc. of water, the liquid boiled 5 minutes, 5 drops of commercial formaldehyde added, the liquid boiled for 2 or 3 minutes longer, allowed to stand for 5 minutes, treated with 5 cc. of 1 per cent. acetic acid, shaken and the pulverulent precipitate collected on a tared filter. The precipitate is washed with water, extracted with acetone, dried at 70° to 80° and weighed. The casein determination is similar.

Blood, Glucosides.—Carlson (*Z. physiol. Chem.*, **48**, 69) stated that 3 per cent. hydrogen peroxide is to be preferred to ozone in turpentine oil for the guaiac blood test, as it gives a sharper and more certain reaction. Schumm (*Ibid.*, **50**, 374) disagreed with this. Horoskiewicz and Marx (*Berl. klin. Wochschr.*, **43**, 1156) observed that 10 to 15 per cent. quinine solution is a good extracting agent for old blood flecks, giving a brown yellow solution with a characteristic absorption band between C and D (wave lengths 628 and 596) instead of the original oxyhemoglobin bands. Eight per cent. quinine solution mixed with the blood in ratio 2:4, heated slowly and gradually to boiling and treated after cooling with 2 to 3 drops of fresh ammonium sulphide solution will give with normal blood a dirty brown-green, but if the blood contain carbon

monoxide it stays carmine-red. Neisser and Sachs (*Ibid.*, **42**, 44; 43
detected human blood by the use of specific sera. If human serum
mixed with an antiserum obtained by treatment of rabbits with hu
serum a mixture is obtained which is capable of interaction. If a se
hemolysin be added, it must remain inactive. Only human and a
sera cause cessation of hemolysis in this case; all others have shown th
selves inactive. Blood spots 3 months old on linen gave the react
Rabbit serum (0.25 cc.) is placed in the liquid to be tested for hu
blood and mixed with the antiserum (prepared from rabbits tre
previously with human serum), the mixture allowed to stand for 1 h
at 37°, then 1 cc. of 5 per cent. sheep blood emulsion added and
stand again at 37° will give proof of the presence of human bloo
hemolysis fails to appear. It is prevented by the interference of 0.
cc. of human serum and even 0.000,001 and 0.000,0001 cc. can be dete
by distinct differences in the hemolytic action. The method is at l
as delicate as the detection by precipitation. Piorkowski (
pharm. Ges., **16**, 226) observed that the hydrocele liquid gives coag
tion with human but not with cow's milk. Every clear human b
liquid shows this reaction. Cow's milk reacts similarly with cattle se
The hydrocele liquid gives soon with human blood a red precipi
while other bloods dissolve; only homologous bloods are precipita
heterologous are dissolved. Sarda and Caffart (*Compt. rend.*, **143**,
found that if a drop of blood solution be evaporated slowly on a mi
scope slide, then treated successively with a drop of chlorine water,
of pyridine and one of ammonium sulphate solution, many chlorhe
tin crystals, rhomboidal rods of varying sizes isolated or in groups o
intense brown-red or bright red color, appear. At the same time
intense red hemmochromogen crystals form in varying numbers in
tuft and brush shapes. Van Itallie (*Pharm. Weekblad*, **43**, 27, 33;
Ber. pharm. Ges., **16**, 65) found that the blood of men and apes
tained catalyzers even after being heated to 63° for 1/2 hour.
of blood (1:1000) were so heated, then cooled to 15° and mixed
3 cc. of 1 per cent. neutral hydrogen peroxide solution when the b
of men and apes liberated oxygen while that of horses, cattle, sw
goats, sheep, rabbits, rats, hares, hens, doves, bony fishes and frogs
not. Woman's milk too, giving unheated 24.8 cc. of oxygen, when heat
the same way for 15 minutes gave 18 cc., 45 minutes 7.5 and 60 min
4.0 cc. of oxygen. The conclusions to be drawn from the above
opposed by Arnold (*Apoth. Ztg.*, **21**, 220) and upheld by Van It
(*Ibid.*, **21**, 230).

Bread, Flour.—Pohl (*Z. angew. Chem.*, **19**, 668) determined alc
in freshly baked bread by distilling, after addition of water to pre
burning, in portions of about 1 kg. The united distillates from al
4.5 kg. were several times redistilled, each time after saturation with
dium chloride, only a part being distilled. The last time the disti
was saturated with calcium chloride and a part distilled off. F
the density determination in the first 50 cc. of this the alcohol was
culated. It was then salted out with potash, distilled and conve
into ethyl iodide for identification. 0.0744 and 0.0830 gram were fo
in white bread prepared from leaven, 0.0508 and 0.0547 gram in
from compressed yeast. Marion (*Ann. chim. anal. appl.*, **11**, 134)

termined gliadin by digesting 10 grams of flour with 50 cc. of alcohol (73° French) in a closed flask at 40° to 45°, shaking frequently, cooling to 15° to 20°, decolorizing with 0.8 gram of animal charcoal, filtering and polarizing. The percentage of gliadin is equal to the reading in minutes multiplied by 0.0722. Shaw (THIS JOURNAL, **28**, 687) tested bleached flour by boiling 1 kg. of it for 4 hours with 95 per cent. alcohol, evaporating the filtrate and wash alcohol nearly to dryness, and extracting the residue with a mixture of equal parts of alcohol and ether. This was evaporated to a syrupy consistency, allowed to dry in a thin film on the inside of the dish and a drop of a solution of diphenylamine in sulphuric acid caused to flow over the surface. The drop called forth a blue color in bleached flours, none in unbleached, the color being due to higher oxides of nitrogen. Gastine (*Compt. rend.*, **142**, 1207) gave a new method for the analysis of flour and the detection of rice in wheat flour. The flour was moistened with a solution of coloring matter, the mass dried carefully, heated for a few minutes at 110° to 130° and then investigated under the microscope in a drop of cedar oil or Canada balsam. The hilum of the starch kernel, at least of some forms of starch, shows in the form of red points ("Punktierungen"). The polyhedral starch kernels of rice give a plain, relatively large reddish hilum, the wheat starches seldom show one. Various blue, green, brown and orange coal tar colors were used, the most suitable concentration being 0.05 gram per 100 grams of 33 per cent. alcohol. One to 2 per cent. of rice flour can be detected with certainty. Maize and buckwheat starch granules behave like that of rice, and many other starch granules like those of the wheat.

Wine.—Billon (*Ann. chim. anal. appl.*, **11**, 127) observed that the total alkalinity of wine ash as ordinarily determined and the alkalinity of the ash of salts precipitated from wine by an alcoholic ether mixture always lie close together but the difference is never negative; for 100 cc. calculated as sulphuric acid it is about 0.01 and never exceeds 0.02 gram. But if the wine contain free sulphuric acid the alkalinity of ash of salts precipitated by the mixture remains unchanged while the total alkalinity is lowered and the difference becomes negative. This is the best test for free sulphuric acid in wine. With wines containing much calcium sulphate it is necessary to add potassium chloride to take care of the tartaric acid. The same author (*Rev. intern. falsific.*, **19**, 57) gave also a method for the determination of glycerol in wines. 50 cc. of an unsugared wine are concentrated to 15 cc., 10 per cent. calcium hydroxide added in slight excess, and the mixture evaporated to sirupy thickness. The cooled residue is washed with absolute alcohol and then with absolute ether completely into a 100 cc. flask and filled with the latter to the mark. All except glycerol is precipitated. An aliquot portion of the filtrate is evaporated, dried and weighed; the residue is pure glycerol. With more than 10 per cent. sugar an amount of slaked lime equivalent to the sugar content is added to the 15 cc. concentrate, the whole evaporated to sirupy thickness and the residue extracted 7 or 8 times with 10 cc. of alcohol each time, cooled and made up to 100 cc. An aliquot portion of the filtrate is evaporated, the residue extracted with alcohol and ether and the determination carried out as above. Cordier (*Bull. sciences pharmacol.*, **13**, 79)

tested wines for poisonous substances by lowering the alcohol content to 8 per cent., adding 25 grams of sugar per liter, introducing a colony of wine yeast and letting the liquid stand in a well stoppered bottle for 8 days. The pressure developed and the gas evolution give with some practice without further test the grade of activity and the increase of the yeast. If the wine contain any poisonous substance, it cannot be worked into a sparkling wine. Primary potassium sulphate hinders the test when present in considerable amount only, but traces of fluorides and other poisonous substances are enough. *Mycoderma vini* and *M. aceti* appear to be still more sensitive. Ross and Mestrezat (*Ann. chim. anal. appl.*, **11**, 41) determined the volatile acids of wine by distilling 20 cc. under diminished pressure, repeating the distillation twice, adding 20 cc. of water each time. With lactic acid present, about 5 cc. must be left in the flask each time, otherwise the wine can be distilled almost dry without danger of decomposition. The volatile acids may be titrated in the distillate using phenolphthalein or determined by difference between total acidity and non-volatile acid content. Vitali (*Vortrag VI. Internat. Kong. angew. Chem. Rome*, 1906; *Boll. chim. farm.*, **45**, 701) found that toluene extracts only salicylic acid from aqueous and alcoholic solutions. The evaporated toluene extract may be taken up with water and tested with ferric chloride or a solution of copper sulphate so dilute that it is colorless. If the solution tested by the latter substance be evaporated to dryness the residue is green, which is not true without the acid. The test may be used on wines and foodstuffs. Schmidt (*Z. Nahr.-Genussm.*, **11**, 386) distinguished between fermentation vinegar and "vinegar essence" by making the sample alkaline with caustic soda, evaporating an amyl alcohol extract, adding water and a little sulphuric acid and treating with iodine-potassium iodide solution. If the mixture is unchanged the vinegar is "essence"; if a cloud or precipitate appears, it is fermentation vinegar. Very small amounts of fermentation vinegar are tested as above in 100 cc. of distillate from sample.

Fibers in Mixed Weaves.—Lecomte (*J. pharm. chim.* [6] **24**, 447) gave a method which makes it possible to distinguish and to count with a magnifying glass the threads of different fibers in mixed weaves. It consists in diazotizing the silk and wool which contain each an amino group and to couple on a phenol group in alkaline solution. Wool contains also sulphur and so by simultaneous action of an alkaline plumbite solution, lead sulphide is formed, concealing the azo color. Plant fibers contain neither of these substances and remain unchanged. One decimeter of decolorized weave is put into 30 cc. of 10 per cent. nitric acid 30 cc. of 5 per cent. aqueous nitrite solution added during 3 minutes gradually and with stirring, allowed to stand 10 minutes, washed for 2 minutes with water, pressed out and cut into 2 pieces. Over one is poured 40 cc. of β-naphthol plumbite solution (50 grams of caustic soda in 500 cc. of water, 25 grams of lead acetate in 300 cc. of water slowly added and 5 grams of β-naphthol added to the clear liquid); the other piece is treated with 40 cc. of resorcinol-plumbite solution (2 grams of resorcinol in place of the naphthol). The weaves are washed after 1 hour at not above 20° with running water for 15 minutes, placed for 5 minutes in 100 cc. of 0.5 per cent hydrochloric acid, washed again for an hour with running water,

pressed out between white filter papers and dried in the dark. Silk will be colored rose-red by the β-naphthol solution, orange-yellow by the resorcinol, the wool black by both, while the plant fibers will remain white.

A portion of the work for this review was done in the library of the department of chemistry of Cornell University, through the courtesy of Professor L. M. Dennis, for which the writer desires to express his thanks.

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INTER-RELATIONS OF THE ELEMENTS.[1]

BY HERBERT N. MCCOY.

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The history of chemistry from the first to the sixth decade of the 19th century shows all too clearly how unsuccessful were the attempts of Dalton and of his contemporaries and successors to fix the atomic weights of the elements by means of arbitrary rules regarding the numbers of atoms which unite with one another, even when these rules were supplemented by knowledge of chemical behavior. Consistent results were obtained only by the aid of the auxiliary hypothesis of Avogadro; which, proposed in 1811, almost unappreciated until after its reanimation by Cannizzaro in 1858, to-day is the corner-stone of the magnificent structure of which the atomic hypothesis is the foundation. Between the physical and chemical properties of the elements and their atomic weights, fixed by means of the hypothesis of Avogadro, there are, as is well known to every chemist, the most fundamental relationships. Of these relationships none is perhaps more significant than that discovered in 1819 by Dulong and Petit. This law supplemented by the relations discovered by Neumann and by Kopp means, simply, that for solid substances, the atoms of all elements, either free or combined, have approximately the same capacity for heat. A few months ago Lewis showed that atomic heats at constant volume are much more nearly constant than the ordinary values, which refer to constant pressure.

During the fifty years following Dulong and Petit's discovery many other relations, more or less quantitative, were found between the properties of elements and their atomic weights; all these relationships were correlated, in 1869, in the Periodic Law of Lothar Meyer and Mendeléeff, which may be concisely summarized in the statement that, in general, the properties of elements are periodic functions of their atomic weights. The comprehensive nature of the law is best appreciated when we remember that these properties include chemical nature, valence, atomic volume, hardness, thermal expansion, crystalline form, conductivity for heat and electricity, melting-point, boiling-point, spectral wave-length and ionic mobility, as well as other properties of less importance. What could illustrate more forcibly the validity of this great law than the startling coincidence in properties of the element, germanium, discovered by Winkler in 1886, and the hypothetical eka-silicon described by Mendeléeff sixteen years earlier, or the equally accurate predictions of the same famous chemist concerning eka-boron and eka-aluminium.

[1] Read at the Chicago meeting of the American Chemical Society.

Very early in the history of the atomic hypothesis, in 1815, to be exact, Prout, a London physician and dilettante in chemistry, observed that the currently accepted atomic weights were, for many elements, exactly or very approximately whole numbers, the atomic weight of hydrogen being taken as unity. Prout contended that all atomic weights should be whole numbers and suggested as the explanation that the elements were composed of hydrogen in various stages of condensation. These views were vigorously opposed by many who were best qualified to judge; Berzelius, especially stoutly denied that the fractional values could be wholly due to experimental error. Later, Stas, whose monumental work on atomic weights was largely inspired by a desire to settle this vital question, convinced himself and also the chemical world in general that Prout's idea was fallacious; at least as to the atomic weights being whole numbers. And this conclusion is strongly confirmed by all the beautiful work of more recent years upon atomic weights. Yet the fact that the values found on the basis of oxygen equal 16, are, in so many cases, so very near whole numbers, must have some far-reaching significance. Calculations by Strutt, based on the theory of probability, have shown that the chances are only about one in a thousand that any set of numbers, assigned purely at random, would differ from whole numbers by so little as do the atomic weights.

From the critical consideration of all the evidence of the sort to which reference had been made, one may safely say that there was abundant reason for the belief that the elements are but various modifications of a primitive substance; *but, the case was not yet proven.*

Far from being novel, the idea of the unity of matter, with the attendant possibility of transmutation, antedates the whole science of chemistry. True it is, of course, that the ancient and medieval views had other bases than the facts which we have been considering; was not the transmutation of a base metal into gold a far simpler change (apparently) than many chemical and metallurgical transformations with which men were even then familiar? To the alchemist the argument was convincing and the goal alluring; and with enthusiasm worthy of a twentieth century "promoter" he often, in bombastic and ambiguous terms, described as accomplished that which existed only in his imagination.

Before the close of the 18th century, however, attempts at transmutation were recognized as futile and one thing appeared certain, even at that time; the elements were not to be disintegrated or altered by such chemical processes as those which served to decompose their compounds. Most of the foregoing facts and arguments are well known to every chemist, since they constitute important chapters in the history of our science. I have merely touched upon them in order to lend perspective to that which is to follow.

During the past eleven years enormous advances have been made along entirely new lines, in the knowledge of the interrelations of the elements and the nature of matter. This new knowledge had its origin in the discovery by Becquerel, in 1896, of the radiations emitted by uranium. It was found by Becquerel that all uranium compounds send out rays capable of affecting a photographic plate through light-proof paper and also of enormously increasing the electrical conductivity of air, by ionizing it. Schmidt, and independently Mme. Curie, found that all

compounds of thorium produce similar rays. Scientists will never forget the intense interest taken in the discovery by the Curies, of radium, a substance which possessed the properties of uranium and of thorium augmented more than a million-fold. There were also new properties: powerful physiological effects, evolution of light and even of heat, it having been found by Curie and Laborde that the temperature of a tube of radium is always perceptibly above that of its surroundings. Here then was a most marvelous result; the continuous and seemingly undiminished production of energy by a portion of matter, which appeared to suffer no chemical change. It even seemed as if a source of perpetual motion had been found.

It was soon clearly established that the activity of radioactive substances was not due to the excitation of any *known* radiation. Some scientists, however, including Lord Kelvin, Becquerel and the Curies, imagined, as the source of the observed energy an unknown cosmic radiation, which was intercepted and transformed by the radioactive body: the elevation of temperature of radium above its surroundings being, according to Kelvin, analogous to that of a piece of black paper in a bottle exposed to sunlight.

The solution of the mystery of radium is largely due to Rutherford and his colleagues. There were two main problems (1) the nature of the radiations, and (2) the nature and cause of radioactivity. The radiations were found to be of three sorts, called the α-, β-, and γ-rays. The nature of the β-rays was first established. The photoactivity is chiefly due to these rays; they readily penetrate light-proof paper; are easily deflected by a magnetic or an electric field, and in such a direction as to show that they are negatively charged. In this respect, as well as in many others, the β-rays closely resemble cathode rays, which latter have been shown to consist of particles of negative electricity, called corpuscles. These corpuscles, which are shot out from the cathode with 1/10 of the velocity of light, have inertia, due to the moving electric charge; and having inertia, they have mass. The mass of a corpuscle is very small; about 1/1000 that of an atom of hydrogen. The β-rays seem to differ from the cathode rays only in having greater velocity. The γ-rays are apparently very penetrating X-rays; and just as the latter are produced by the cathode rays, the former are produced by the β-rays.

The α-rays are quite different: they are unable to penetrate a single sheet of writing paper; but they are the chief cause of the ionization of the air and the elevation of temperature. Rutherford has shown that the α-rays consist of positively charged material particles, each having a mass 2 (or 4) times that of an atom of hydrogen and moving with 1/3 the velocity of light. It was now readily understood that the kinetic energy of the rays was the proximate cause of the observed evolution of heat by radium.

The counterpart of the phenomena of the rays was found in the change which occurred at the same time in the active substance itself. Crookes had observed that by treating uranium nitrate solution with an excess of ammonium carbonate a minute insoluble precipitate remained; this precipitate, called uranium X, was found to possess practically the whole of the photoactivity of the uranium from which it had been separated. Rutherford and Soddy precipitated thorium with ammonia and obtained

from the filtrate a trifling residue called Thorium X, which possessed a large share of the original activity. The activity of the ThX decreased gradually with time; in 4 days the activity was reduced to 1/2, in 8 days to 1/4. The loss of activity occurred according to the exponential law, or, as the physical chemist would say, the change was that of a first order reaction; in each unit of time a fixed fraction of the remaining activity disappeared. To some scientists it did not appear remarkable that the radioactive principle of uranium or thorium could be separted by a chemical process; in fact the original activity of these elements was "explained" as due to the presence of these highly active "impurities." Nor did the loss of activity by UX or ThX, considered by itself, seem extraordinary; it might be likened to loss of temperature by a cooling body.

But a most extraordinary thing was discovered by Rutherford and Soddy, in the further study of this same thorium experiment. The thorium from which ThX had been removed had, at first, only about 1/3 of its original activity; but in just that measure in which the separated ThX lost its activity, that of the thorium itself returned; until, after a period of several weeks, the thorium had entirely regained its original activity, while the ThX had become inactive. A repetition of the treatment with ammonia now yielded a new portion of ThX equal in amount to that first extracted! The behavior of UX was similar. Rutherford and Soddy then announced their now celebrated Disintegration Hypothesis: the radioactive atom is a complex system, made up of corpuscles and α-particles, in rapid orbital motion; of such systems some, in the course of time, became unstable and disintegrate, the corpuscles and α-particles resulting from such atomic disintegrations constitute the rays, the kinetic energy of which existed previously in the atom. The residual portion of the atom, after the escape of a corpuscle or an α-particle, constituted an atom of a new substance (*e. g.* ThX), which atom might have even less stability than the original.

In all, over 20 distinct radioactive substances are now known. These constitute three series, in each of which each member produces, by its radioactive disintegration, the following member. The evidence in the case of each change is just as clear as in that of thorium and thorium X. One case in particular, that of the formation of radium from uranium, is of especial interest. It has been shown in two different ways that radium and uranium are always associated in minerals, and, moreover, in a perfectly fixed proportion, as demanded by the hypothesis that the one is the product of the other. Further, uranium minerals freed from radium by chemical processes, slowly but surely reproduce the latter substance.

The chemical and physical properties of radium and its salts clearly show it to be a member of the alkaline earth family; its atomic weight is according to the latest determination of Mme. Curie, 226.5, assuming the elements to be bivalent. The formation of radium by uranium was then a clear case of the transmutation of one element into another whatever might be thought of such changes as that involving the production of ThX.

The properties of the α-particle led Rutherford and Soddy to suggest, in 1902, that it might be an atom of helium. In 1903 Ramsay and Soddy

were able to show that radium emanation actually does produce helium in the course of its spontaneous disintegration; this observation has, since then, frequently been confirmed. The formation of helium seemed to be another real transmutation; since the element radium undoubtedly produced the emanation which yielded in turn another element, helium.

If now uranium gives ultimately radium, what is the final product of the disintegration of the latter? Boltwood believes it to be lead, since he finds that all uranium-radium ores contain notable amounts of lead. In the disintegration of an atom of radium five distinct α-ray changes occur. If each produces one α-particle, with atomic weight of 4, the final product of radium should have an atomic weight of $226.5 - 20 = 206.5$, whereas the atomic weight of lead is 206.9.

There is now no shadow of doubt that the rate of radioactive change is entirely independent of the form of chemical combination of a radioactive substance; temperature is also without influence; a given transformation occurs at precisely the same rate at the temperature of liquid hydrogen and at white heat. It thus appears that radioactive change is a natural process which is entirely beyond man's control, and important as is the establishment of this fact, the discovery falls far short of being a complete solution of the problem of the transmutation of the elements.

A further step in this direction seems to have been taken within the past few months, however, by Sir William Ramsay. The alchemist in his attempts to alter the elements, could apply only the forces of moderate heat and chemical affinity. The chemist of the 19th century could command enormously greater ranges of temperature as well as powerful electrical forces; all these means were likewise without avail. And now Ramsay has tried a new force, that of radioactive radiations: corpuscles and particles of matter, both electrically charged, projected with almost inconceivable velocity. The results of the experiments of Ramsay and Cameron may be stated very briefly; radium emanation acting on water produces neon; while with a solution of copper nitrate it produces argon; and even the copper itself appeared to be attacked, for when the latter element was removed by means of hydrogen sulphide, the filtrate was found to contain lithium. A blank experiment, in which the radium emanation was omitted but all other conditions remained precisely the same, yielded no trace of lithium. The formation of lithium from copper has been observed four times by Ramsay and though, as he writes in a private communication, "he was loth to believe," yet he "had to chronicle the results after four repetitions." The importance of these facts, provided they are not due to some spurious cause, needs no comment. In this connection it occurred to me that radium emanation, or in general radioactive radiations, might act on copper in the solid state; if so, uranium-radium minerals which contain copper should contain lithium also. For another purpose I had, more than a year earlier, separated a sample of pitchblende into its principal constituents. There was a considerable quantity of copper; there was also a solution which could contain only alkali and ammonium salts. It was but the work of an hour to examine this solution for lithium; in the spectrum the characteristic red line of lithium was next in brilliancy to that of sodium! Later, from one to two grams of four other uranium minerals, including sam-

ples of pitchblende, carnotite and gummite, from widely separated localities, were examined for copper and lithium: all contained lithium and all but one contained copper. The presence of lithium in a mineral free from copper may be explained upon the supposition that the transmutation of the latter metal had been completed.

The view that the atom is a complex system made up of negatively charged corpuscles and positively charged α-particles has been made the subject of extensive mathematical studies by J. J. Thompson. Thompson's hypothetical atom is a system composed of rings or shells of corpuscles in a uniform sphere of positive electrification. The electropositive or negative nature of atoms, their chemical affinity as well as their dual valence toward hydrogen and oxygen are all most beautifully and at the same time simply explained by the behavior of such imaginary systems, the properties of which vary periodically with increasing number of corpuscles and so fulfil another indispensable requirement of any hypothetical atom. Numerous other properties of matter also receive a satisfactory explanation in terms of the new hypothesis: among such are the conductivity of metals for heat and electricity, bright line spectra and the Zeeman effect. That the corpuscular theory is the last word on the nature of matter, none will contend: Thompson himself writes, "The theory is not an ultimate one; its object is physical rather than metaphysical. From the point of view of the physicist, a theory of matter is a policy rather than a creed; its object is to connect and coordinate apparently diverse phenomena, and above all to suggest, stimulate and direct experiment."

The view just given of the nature of the atom accounts also for its radioactivity. A system of revolving corpuscles of negative electricity would slowly radiate energy, at an almost infinitesimal rate it is true; but the final result would be to produce in the system a condition of instability which would cause its partial disintegration and rearrangement. Is then all matter undergoing evolution? That is the question which cannot be positively answered at present. And yet there is much evidence that many elements are faintly radioactive. Such activity may be either intrinsic or due to minute amounts of known highly active substances. Radioactive matter is easily extracted from the air by means of a negatively charged wire exposed out of doors, as first shown in 1901 by Elster and Geitel. The rate of change of this active matter indicates that it is chiefly the excited activity, Ra A, B and C, resulting from the disintegration of radium emanation. A simple experiment which I recently tried shows the correctness of this view. Air was liquefied and about a liter of the liquid was allowed to evaporate, and the last portion was examined for radioactive emanations. A considerable activity was found, the rate of change of which plainly indicated the presence of radium emanation together with small amounts of other active matter. The excited activity, which is deposited everywhere by the radium emanation contained in the air, is certainly the cause of a portion of the observed activity of common things. Nevertheless, at least one common element, potassium, seems from the studies of Campbell to possess slight intrinsic activity.

On the other hand, it is found that α-particles having less than a certain minimum velocity are unable to produce ionization of the air. It

is therefore quite possible that some atomic transformations may occur which do not show radioactive phenomena, the initial velocity of the α-rays being, in such cases, below the minimum. Such change might occur at rates far greater than that of uranium and still be impossible of detection in the course of a lifetime by gravimetric or even probably by spectroscopic methods, since in the case of uranium the rate of change is so slow that no more than 0.001 per cent. disintegrates in 10,000 years; and yet the ionization method of recognizing α-radiations is so surpassingly delicate that one may detect with certainty the activity due to a single milligram of uranium in any form of combination!

In conclusion, it may be said that while the work of the 19th century produced abundant and varied evidence that between the elements there exists the most intimate interrelationships, the researches of the past few years of this new century have shown the fundamental significance of these relationships and lead us to the conclusion that the elements may no longer be considered immutable; that matter is probably of but a single sort, of which our commonest elements represent the more stable forms, which have resulted from a process of natural evolution.

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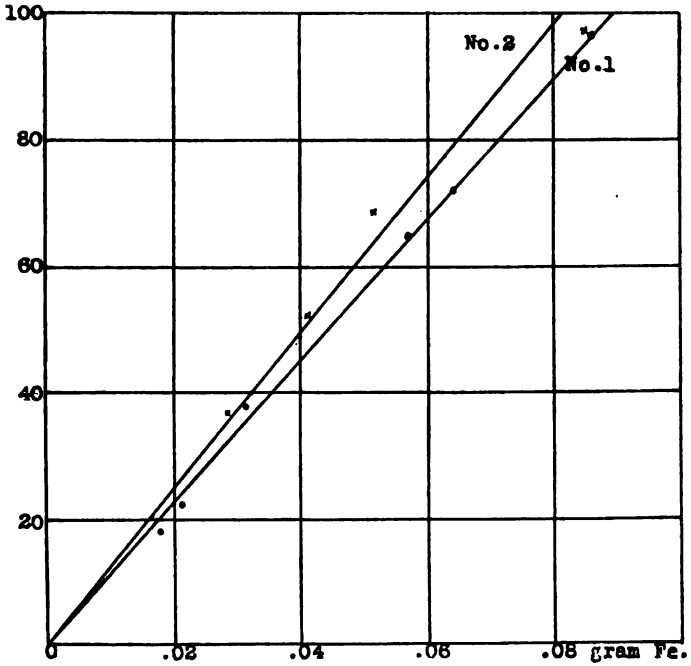
CORRECTION.

Plot and footnote omitted by mistake from article on "The Corrosion of Iron and Steel," by W. H. Walker, A. M. Cederholm and L. N. Bent, in September number of this Journal, 1907. The plot should be inserted to



ccompany page 1260 and the footnote[1] added to "2" at botto
age 1255.

Plot showing the relation between speed of corrosion of iron in water an
artial pressure of the oxygen in the carbon-dioxide-free atmosphere.

EXPERIMENTAL DATA.

No. 1.		No. 2.	
Percentage oxygen.	Grams iron dissolved.	Percentage oxygen.	Grams iron dissol
18.2	0.018	20.0	0.017
21.8	0.021	37.1	0.029
28.0	0.031	52.2	0.041
64.5	0.057	68.7	0.055
72.1	0.064	97 2	0.085
97.0	0.086	..	.

[1] Concerning the passivity imparted to iron by chromates, see A. S. Cus
Bulletin No. 30, Office of Public Roads, U. S. Department of Agriculture.

NEW BOOKS.

n Elementary Study of Chemistry. By WILLIAM MCPHERSON AND WILLIA
WARDS HENDERSON. Revised edition. viii + 434 pp. Ginn & Com
Boston. (No date on title page.) Price, $1.25.

This is an important book for it is manifestly destined to be w
ised in high schools and small colleges and thus to have much influ
ipon education in chemistry. In the preface the authors say '
ave made a consistent effort to make the text clear in outline, si
n style and language, conservatively modern in point of view and
oughly teachable." It is a pleasure to be able to offer congratula
ipon the good measure in which these aims have been attained.

The elementary facts of descriptive chemistry, chosen with ac
ble judgment, are presented clearly and interestingly. Even in
atter part, treating of the metals and their compounds, material
o condense itself to a tedious catalogue of substances and prope
nterest is well kept up by judicious interpolation of applications
hort digressions. The simplicity and directness of the language
ts hold on the attention remind one of Professor Remsen's texts.

The treatment of the theories is less praiseworthy. The atomic th
s stated on page 62, immediately following the law of multiple pr
ions. The reviewer believes this theory should be reached cauti
nd laboriously through not only the laws of definite and multiple
ortions by weights, but also Gay Lussac's law of combining vol
nd Avogadro's molecular theory. These latter subjects are not
idered until pages 194 and 226 respectively.

The authors do not insist enough upon the uncertainty inheren
ll theories. On the contrary they repeatedly make the serious
ake of using theory as solid, rock-bottom fact upon which to b

As one illustration of this we may cite the definition on page 116: "The valence of an element is that property which determines the number of the atoms of another element which its atom can hold in combination." If there is one place where theory has absolutely no business, where if present it does maximum harm, that place is in a definition. The dissociation theory also is brought in early (p. 99), on an inadequate experimental foundation, and is utilized as fundamental fact. Thus on page 107 we have the definition: "An acid is a substance which produces hydrogen ions when dissolved in water or other dissociating liquids."

Much time and thought must have been given to composing the numerous compact definitions, but even if they were not, many of them, open to the above criticism, it is doubtful if they are wholly desirable. Such brief statements are convenient from a teacher's point of view, furnishing knowledge in tablet form, which he has but to prescribe, two or three tablets daily five times a week, and go off about other business. Thus drugged the student makes a fine show when put through his paces by his trainer, but let an unfamiliar voice ask the questions in different form or, not satisfied with an accurate recital of the well committed phrase, press for further information, and great is the resultant distress, confusion or irritation as the case may be.

A book is not made modern by including the dissociation theory, the conception of chemical equilibrium, etc., alone. The real test is in the way theories are utilized. If they are taught didactically (by far the easiest way to teach them), the student is almost sure to attribute to them the finality of mathematical demonstrations, and the book is "conservative," *i. e.*, old-fashioned. If they are brought out as the best suggestions we have yet been able to make regarding branches of knowledge still in a state of flux, debatable and in no sense certain, the book is modern. The good old-fashioned book sends to the universities students much surer of many fundamental propositions than their teachers venture to feel, but with atrophied thinking faculties. The more difficultly teachable, modern book develops alert and critical but humble individuals with an almost painful appreciation of the limitations of human knowledge and a realization that the most far-reaching, most difficult, least understood problems of science lie at the beginning, in elementary chemistry. Judged by the above criteria the book under review is more "conservative" than "modern." It must be acknowledged that only a minority of teachers believe that it is better to give even immature high school students the undisguised truth, interlarded though it must be with many a "we don't know," and "we can only surmise;" and possibly this minority is mistaken. But it is also barely possible that the

high value set on "teachableness" is due, sometimes, as much to consideration for self as for students.

But the reviewer does not wish to be misunderstood, the good points of the book overbalance those which do not happen to coincide with his own, perhaps peculiar, notions, and the proof of his appreciation is that he intends to recommend it as one of the two or three best elementary texts known to him. S. LAWRENCE BIGELOW.

Die Kathodenstrahlen. By G. C. SCHMIDT. Prof. Phys. Univ. Königsberg. Second editon. Braunschweig: F. Vieweg und Sohn. 1907. 127 pp. Price, Mark, 3.60, bound.

This monograph, which forms No. 2 of the collection, Die Wissenschaft, gives a clear and concise account of our knowledge of the electric discharge in evacuated vessels. The book is intended for the non-specialist; the use of mathematics is almost wholly avoided; yet, by means of well chosen illustrations and ingenious analogies, the reader is easily led to an accurate understanding of this most fascinating subject. The topics treated include the nature of light and the luminous ether; the cathode rays, their production and behavior, together with an excellent critical discussion of the various hypotheses regarding their nature; the nature of the electron or corpuscle, its velocity, charge and mass; the Zeeman effect; the canal rays, etc. This little book is a welcome addition to the semi-popular literature of the corpuscle, the primitive unit of which all matter seems to be built up. HERBERT N. MCCOY.

The Microscopy of Technical Products. From the German of Dr. T. F. Hanausek. Translated by Andrew L. Winton, Ph.D., with the collaboration of Kate G. Barber, Ph.D. New York: John Wiley & Sons. 1907. 8vo, xii+471 pages, 276 illustrations. Price, $5.00.

This book which has enjoyed a well established reputation in the original is now presented to English readers in the work of Dr. Winton. While not dealing with chemical methods of identification, except incidentally, it nevertheless must possess no little interest for those chemists who are engaged in various lines of expert testing work in which recourse to the microscope is often absolutely necessary. The portion of the book which will be found the most useful to analytical chemists are the chapters on the starches, stems and roots and fruits and seeds. These are clearly written and illustrated.

The rapid extension of the national and state food and drug laws makes the kind of knowledge contained in this book especially valuable at the present time. The translator is at the head of the Government Food and Drug Laboratory in Chicago and has had a long experience in the line of work discussed in the book. From this practical experience he has been able to make more than a translation of it, as the numerous notes attest. The illustrations, essential in a work of this character,

are especially good. On the whole, the book can be heartily recommended. J. H. LONG.

Introduction to the Theory and Practice of Qualitative Analysis by Solution. By F. W MARTIN, PH.D., Lynchburg, Va. J. P. Bell Co. 1907. pp. 64. Price, $0.75.

In this small guide to qualitative analysis the first three chapters are devoted to general matters related to the theory of solutions, such as osmosis, vapor pressure, ionization, chemical equilibrium, hydrolysis, etc. The fourth and fifth chapters deal with the classification of the bases and acids into groups. A few reactions of the members of each group are given. Chapters 6 and 7 give the systematic procedure for the identification of acidic and basic ions. Chapter 8 contains a list of 27 exercises to be carried out according to the directions given in the preceding chapters.

The appendix contains a list of reagents with brief directions for making them. It is not intended that the treatise should be used without the personal instruction of the teacher. As the author says in the preface, "He (the instructor) is the one indispensable feature of a laboratory." EDWARD H. KEISER.

Electro-Analysis. By EDGAR F. SMITH. 4th edition revised and enlarged, with 42 illustrations. Philadelphia: Blakiston's Son & Co. 1907. Price, $2.50 net.

Since the last edition of Professor Smith's book was published in 1902, the rotating electrode has been introduced into electro-analysis, with the result that in many cases the time required to complete an electrolysis has been reduced from hours to minutes. The present work is the first to give full details of the conditions under which satisfactory results may be obtained with this new tool, and is thus the only really "up-to-date" treatise on electro-analysis in existence.

Many of the new methods have been worked out in the laboratory of the author, and their accuracy and speed are attested by numerous trial analyses; particularly interesting are those in which both anion and cation are determined in a single operation with mercury cathode and silver anode.

In many instances, no doubt, the slower methods will still remain in use—to leave the current on over night is a very easy method of making an analysis—and the author has done wisely in retaining the descriptions of the older methods side by side with those of the new. One hundred and thirty pages have thus been added to the book; if in a future edition it should prove necessary to economize space, it might be a good idea to cut out the pictures on pages 64 and 97 in which a milliammeter worth thirty dollars or so is represented as tilted against an accumulator cell filled with sulphuric acid. There are laboratories where a student could get himself into trouble by attempting to carry this suggestion into practice. W. LASH MILLER.

Church's Laboratory Guide. By EDWARD KINCH. D. Van Nostrand Co., N. Y
ed., 1906. pp. 349. Price, $2 50.

This book is largely devoted to the quantitative analysis of ag
tural products. The first edition was published in 1864 and foun
tensive use in Great Britain, India, Italy, Japan, etc. The presen
tion has been carefully revised and largely rewritten and brougl
to date. Part I consists of a general introduction in chemical ma
lation. Part II is devoted to qualitative analysis, especially in re
to those elements of agricultural interest. Part III, comprising
200 pages, deals with the quantitative analysis of agricultural
rials, such as soils, manures, farm crops, cattle foods, dairy pro
bread, etc. The book is clearly written, well arranged and, in
respects, well up to date. We notice that, in common with mos
ropean works, the Babcock method of determining fat in milk a
products (almost exclusively used in America) is entirely ignor
the writer. As a rule, European writers on chemical methods o
cultural analysis do not prepare works that are entirely satisf
for the use of American students in our agricultural colleges. It
difficult to see why this should be so. L. L. VAN SL

Dairy Laboratory Guide. By CHARLES W. MELICK. D. Van Nostrand Co.
1907. pp. 129. Price, $1.25.

This book is intended for use in short dairy courses covering
few months of work. It treats from the standpoint of laboratory
tice a large number of subjects connected with milk and its mar
tions in connection with the processes of butter and cheese makin
preparation of other dairy products. The treatment given to each
is brief and necessarily superficial but is undoubtedly intended to b
plemented by class work with lectures. We question the wisd
using chemical formulas in a book of so elementary a character
students who have studied chemistry little, if at all. The state
are for the most part clear and accurate. The book has no in
serious fault in any book, however small. We notice that the
adheres to the old theory of the cause of mottles in butter, attri
it exclusively to the action of salt and ignoring the essential part
by the presence of buttermilk. On the whole, the book, if pr
used, can be recommended for the purposes intended.

L. L. VAN SL

Annuaire pour l'An 1908. Publié par le Bureau des Longitudes. 16 mo., 95
Paris: Gauthier-Villars. Price, 1 franc 50 centimes (by mail, frs. 1

Nearly one-half of the volume consists of astronomical and geoma
data, one-quarter is physical tables, nearly one quarter chemical
and an appendix contains special articles on the distances of the

stars (G. Bigourdan), solar researches (Deslandres), the observatory of Montsouris (E. Guyon), and obituary notices of M. Loewy and Chas. Trépied. It is impossible to obtain anywhere else so much physical and chemical data for such a small price, and the data given are in the main reliable. The criticism made on previous volumes still holds true on this, *viz.*, that data obtained by famous French scientists continue to be given even where some of them have been proved in error and replaced by better observations by scientists outside of France: *e. g.*, Regnault's determination of the vapor tension of mercury below 100°.

J. W. RICHARDS.

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A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.[1]

PART III: ANALYSIS OF THE ALUMINUM AND IRON GROUPS, INCLUDING BERYLLIUM, URANIUM, VANADIUM, TITANIUM, ZIRCONIUM AND THALLIUM.

BY ARTHUR A. NOYES, WILLIAM C. BRAY, AND ELLWOOD B. SPEAR.

Received January 28, 1908.

Introduction.

This article is a continuation of a preceding one which appeared in an earlier number of this Journal in which were presented the first two parts of this system of qualitative analysis, dealing respectively with the preparation of the solution, and the analysis of the silver, copper, and tin groups.[2] For the purposes of this investigation, for the general considerations underlying it, and for various conventional matters relating to its presentation, the reader is referred to the introduction to the preceding paper.

Although the final form of the scheme of analysis of the groups here considered has been worked out during the past year by the authors of this article, much of the preliminary experimental work, especially that relating to the rarer metals, was carried on by others in this laboratory. It is unfortunately, scarcely practicable to indicate in just what respects each of these investigators has contributed to the final result; but we wish to express in a general way our great indebtedness to Messrs. Howard I. Wood, Bart E. Schlesinger and Charles Field, 3rd, for the assistance which their work has been to us.

[1] Copyright, 1908, by Arthur A. Noyes.

[2] THIS JOURNAL, 29, 137 (1907).

The present publication deals with the analysis of the precipi
ɔduced by ammonium hydroxide and sulphide in the filtrate from
drogen sulphide precipitate. In addition to the seven com
ments (nickel, cobalt, iron, manganese, zinc, chromium and a
ım) considered in almost all schemes of qualitative analysis,
ve included six of the especially important rarer elements, nam
ryllium, uranium, vanadium, thallium, titanium and zircon
ıe portions of the procedure and of the notes referring to these
ments are, however, marked with asterisks, so that they ma
ıdily omitted by any one interested only in the common elemen
The general features of our scheme for the analysis of this solu
ll be most readily comprehended by an examination of the tab
tline presented in Tables VII to IX. The considerations which
l to the adoption of this procedure will be discussed in the next cha
titled "General Discussion," and the detailed process and the
ınations of it will be presented in the following one entitled "
dure and Notes." Later chapters, as in the preceding publica
ll be devoted to the "Test Analyses and to Confirmatory Ex
ents and References."

General Discussion.

(1) With respect to the original precipitation of these elem
ıemes of qualitative analysis differ as to whether ammonium
oxide and ammonium sulphide be used successively with a filtr
tween, or whether they be added together so that all the element
ntained in a single precipitate. The former of these methods
e serious disadvantage that the separation with ammonium
oxide of the trivalent elements, aluminum, chromium and
ɔn, from the bivalent elements, nickel, cobalt, manganese and
ıile satisfactory enough when certain combinations of these elem
e present is not so for other combinations. Thus even a large qua
zinc may be quantitatively precipitated by ammonium hydr
ıen a larger proportion of chromium is present; and manganese
any case be partially precipitated by that reagent owing to its o
ɔn by the air to the manganic state, and it will be completely
ɔitated when phosphate is present in the solution. It is ther
cessary to provide for the detection of zinc and manganese both i
droxide and in the sulphide precipitate; and thus the scheme is
cated rather than simplified by precipitating separately with
ıgents.

We have therefore adopted the plan of a single precipitatio
nultaneous addition of both reagents, provision being made,
er, for observing the effect of the addition of ammonium hydr
ɔne for the sake of the indications which it may furnish. If ca

taken to avoid an unnecessary excess of both the hydroxide and sulphide, all the elements in question are completely precipitated by these reagents even in moderately dilute solution, with the exception of a little of the nickel and a variable proportion of the vanadium. The nickel can be removed from the filtrate by boiling. Even a large quantity of vanadium remains completely in solution when it is present alone; but on the other hand it may be almost completely precipitated, probably as a hypovanadate or vanadate, when certain other elements of these groups are present. Many experiments were made in this laboratory by Mr. Charles Field, 3rd, to devise a practical method of reducing vanadium to a vanadous salt (corresponding to the oxide V_2O_3), in which state it is completely precipitated by ammonium hydroxide. In accordance with the results of Gooch and Curtis[1] hydriodic acid (best in the form of a mixture of ammonium iodide and hydrochloric acid) was found to be the only available agent, but even with the aid of this reagent reduction and precipitation were never quite complete and sometimes did not take place at all. For this reason it was not considered worth while to use this reagent, especially since the vanadium can be removed from the ammonium sulphide filtrate by acidifying, adding ferric chloride and making alkaline with ammonia.

(2) The ammonium sulphide precipitate in all the schemes of analysis known to us is first treated with cold dilute hydrochloric acid, in order to separate nickel and cobalt from the other elements. In spite of the general use of this process, we have become convinced that it does not fulfil the requirements of exact qualitative analysis; for not only is it true, as is generally known, that a considerable quantity of nickel and cobalt dissolves in a mixture of 1 volume of HCl (1.12) with 5 volumes of water when there is a large residue containing these elements, but our experiments have shown that a moderate quantity of either of them (up to at least 5 mg.) may *completely* dissolve and thus escape detection when it was originally disseminated through a large precipitate of iron sulphide. We have therefore eliminated this treatment as a method of separation; and, after adding hydrochloric acid at first to decompose such of the sulphides as it will act upon and to get an indication as to the presence of much nickel or cobalt, nitric acid is added, so as to bring all the elements into a single solution. Incidentally it may be mentioned that our experiments support the view that the fact that nickel and cobalt sulphides, though not precipitated by hydrogen sulphide from a slightly acid solution, yet dissolve difficultly in a much stronger acid, is due to an abnormally slow rate of solution of these sulphides, which are in fact relatively soluble substances, at least in the freshly precipitated state. For these experiments have shown that nearly all of a

[1] *Am. J. Sci.* (4), 17, 45 (1904).

portion of precipitated nickel sulphide dissolves when treated with successive portions of cold dilute HCl (1 volume HCl (1.12) with 5 volumes of water) even when the acid is kept saturated with hydrogen sulphide, and that solution continues to take place even after considerable nickel (30 mg. in 30 cc.) has passed into solution. When, therefore, the surface exposed to the acid is greatly increased, either, by the residue being a large one or by a small residue being left in a finely divided state by the dissolving out of iron sulphide, a considerable quantity of nickel and cobalt passes into solution in a comparatively short time. It is interesting to note that the reverse reaction, the precipitation of nickel sulphide by hydrogen sulphide in acid solution, also takes place very slowly, for Baubigny[1] has observed that in the presence of acetic acid, or of very small amounts of sulphuric or hydrochloric acids, the precipitation is a slow but continuous process.

(3) Having now all the elements together in solution, the next step in our process is to divide them into two main groups by the addition of sodium hydroxide and peroxide, followed by subsequent boiling. This method has been previously applied by other authors to the separation of certain of the common elements, but not, we believe, as a general means of subdivision. These reagents cause the complete precipitation of iron, nickel, cobalt and thallium, as hydroxides of the trivalent form, and of manganese, titanium and zirconium as hydroxides of the quadrivalent form. We shall designate all these elements so precipitated as the "iron group." All the remaining elements, namely, aluminum, beryllium, zinc, chromium, uranium and vanadium, remain in solution in the form of sodium salts of the corresponding acids, namely, as aluminate, zincate, chromate, peruranate and vanadate. We shall designate all these elements so dissolved as the "aluminum group." The separation of the two groups by this process is entirely satisfactory, at any rate, from the standpoint of qualitative analysis, with the single exception that when only 5 or 10 mg. of zinc are present, this may be carried down completely when elements of the iron group (especially manganese) are present in large quantity. This makes it necessary to provide for the detection of zinc in the analysis of the precipitate when it is large, but this is not attended with special difficulty. The use of sodium peroxide has the distinct advantage over that of sodium hydroxide alone, that chromium, uranium and vanadium are taken completely into solution whereby not only a division of these elements between the precipitate and filtrate is avoided, but also the carrying down of zinc into the precipitate is made less common and less considerable.

(4) Since, owing to the possible presence of phosphate, oxalate, or

[1] Baubigny, *Compt. rend.*, 94, 963, 1183, 1251, 1417, 1473, and 1715 (1882), and 95, 35 (1882).

hypovanadate in the original solution, the alkaline-earth elements may be precipitated by ammonium hydroxide and sulphide, sodium carbonate is added with the hydroxide and peroxide, in order to ensure the complete precipitation of these elements (more especially barium) with the iron group. The presence of phosphate and carbonate does not affect at all the separation of the elements of the aluminum and iron groups from each other.

(5) The separation of the elements of the aluminum group from each other is very simple when only the common elements, chromium, aluminum and zinc, are to be provided for, and the process recommended below for this case offers no original features. It consists in precipitating the aluminum hydroxide from the solution with ammonium hydroxide after acidifying with nitric acid, the chromate in the filtrate with barium chloride after acidifying with acetic acid, and the zinc with hydrogen sulphide in the filtrate from the barium chromate.

(6) The presence of beryllium does not involve any complication, since it goes with the aluminum in the process just referred to, and can be separated from it as described below. When, however, uranium and vanadium are to be provided for, this process is entirely inadequate, for upon the addition of ammonium hydroxide after acidifying, vanadium divides between the filtrate and precipitate wherever uranium is present, owing to the insolubility of uranyl vanadate; uranium itself will divide owing to the presence of H_2O_2 formed on acidifying the sodium peruranate solution; and vanadium, when present in large amount, again divides upon the addition of barium chloride to the acetic acid solution, owing to the slight solubility of barium vanadate; finally vanadium interferes with the test for zinc with H_2S in acetic acid solution, since a precipitate of sulphur is always formed and sometimes one of black vanadium sulphide. Moreover, the uranium precipitate obtained with ammonium hydroxide will in general be mixed with aluminum, beryllium and vanadium, so that the difficult part of the separation still remains to be accomplished. After much experimenting, guided by the conception that under proper conditions of alkalinity it might be possible to separate the more basic elements, zinc, aluminum and beryllium, from those present as constituents of acid radicals, chromium, uranium and vanadium, it was finally found that this could be accomplished in a hot solution of sodium hydrogen carbonate, provided care be taken to prevent loss of carbon dioxide by heating the solution in an open vessel only to 90°, or better in a closed bottle to 100°. Under these conditions the separation is a fairly satisfactory one. A small amount of uranium may, however, be carried down almost completely when a large amount of aluminum or beryllium is present, making it necessary to test for uranium in the pre-

cipitate. Moreover, when uranium and vanadium are simultaneously present, each in large quantity (about 100 mg.), some uranyl vanadate precipitates, but a large quantity of both elements remains in the solution, so that their detection is not interfered with.

(7) The separation of the zinc from the aluminum and beryllium in the precipitate is readily effected by dissolving it in hydrochloric acid and adding a small excess of ammonium hydroxide. For the separation of the aluminum and beryllium from each other we studied what seemed to be the two most promising methods mentioned in the literature. The first of these was that described by Parsons and Barnes,[1] which consists in boiling for a short time a solution of the two elements to which enough sodium hydrogen carbonate is added to make a 10 per cent. solution, whereby aluminum is precipitated and beryllium dissolved. We found, however, that though this method is satisfactory for the detection of beryllium when a moderate amount of aluminum is present, yet with a large quantity of aluminum (say 100–500 mg.) 2–5 mg. of beryllium are almost completely retained in the precipitate, which may cause it to escape detection, and which at any rate leads to an incorrect estimate of its quantity. The second method investigated was that proposed by Havens[2] which consists in saturating a solution of the chlorides of the two elements in a mixture of ether and strong hydrochloric acid with hydrogen chloride gas, whereby aluminum is precipitated and beryllium remains in solution. It was found that this method gives entirely satisfactory results; even 0.5 mg. of aluminum is precipitated, as $AlCl_3.6H_2O$, provided care be taken to use a sufficient proportion of ether and to saturate completely with the gas; even 100 mg. of beryllium remain wholly in solution, and 0.5 mg. is not carried out with a large quantity of aluminum. This method was, therefore, adopted for the separation, it being supplemented by a confirmatory test for beryllium based on the process of Parsons and Barnes.

(8) The separation of the chromium, vanadium and uranium, which are present together in the filtrate from the sodium hydrogen carbonate precipitate, also required much investigation. It was soon decided that there was more promise of effecting a separation of the first two of these elements in the state of chromate and vanadate, in which they already exist, than in a lower stage of oxidation; and it was found that the lead salts differed sufficiently in solubility in nitric acid to enable 0.5 mg. of chromium to precipitate while retaining 100 mg. of vanadium in solution. A separation based on this fact was therefore adopted. The excess of lead added is subsequently removed by saturating the filtrate with hydrogen sulphide. To avoid the addition and removal

[1] THIS JOURNAL, 28, 1589 (1906).

[2] Z. anorg. Chem., 16, 15 (1898).

of lead when chromium is absent, a preliminary test for chromate with hydrogen peroxide is introduced. The uranium is separated from the vanadium (after oxidation to the vanadic state) by precipitating it as uranyl ammonium phosphate in acetic acid solution—a method that was found to give satisfactory results for the limiting case of a large proportion of uranium and a small proportion of vanadium, and also in the converse case. Vanadium is tested for by making the filtrate strongly alkaline with ammonia and saturating with hydrogen sulphide, whereby a violet-red solution of a vanadium sulpho-vanadate is formed.

(9) We will next consider the analysis of the precipitate produced by sodium peroxide, which contains the manganese, iron, nickel, cobalt, thallium, titanium and zirconium, the alkaline-earth elements, and possibly phosphate. The main problems connected with this were the separation of the manganese from the other elements, that of the alkaline-earth elements from phosphate and that of the titanium and zirconium from the iron and from each other.

(10) In almost all schemes of qualitative analysis it is thought sufficient to test a portion of the precipitate for manganese by fusing it with sodium carbonate or by boiling it with lead dioxide and nitric acid, without isolating the manganese. These color tests give, however, but little idea of the quantity of the element present. Moreover, aside from this objection, the large number of the elements contained in the precipitate in this scheme makes their separation necessary. The one reaction of manganese which seemed in every way suited for this purpose is that frequently employed in iron and steel analysis consisting in the conversion of the manganese into the dioxide by the action of chloric acid and concentrated nitric acid. For this is not only a behavior highly characteristic of this element; but, since the separation is carried out in a strongly acid solution, it might be anticipated that the other elements, which are not oxidizable to insoluble peroxides, would not be retained in the precipitate to an important extent. Our experiments have shown that this is, in general, the case; but one exception has been discovered. It has been found, namely, that titanium, which is quadrivalent like manganese in the dioxide, when present even in considerable quantity (up to 50 mg.) may be completely precipitated with a large quantity of manganese (500 mg.), and that a large proportion, though not all of the zirconium is likewise carried down. The method is, however, otherwise so satisfactory that we have adopted it, special provision being made for this unusual case in a way that need not be described here. The procedure consists in dissolving the whole sodium peroxide precipitate in strong hydrochloric acid, in evaporating with excess of nitric acid, adding concentrated nitric acid and

potassium chlorate, heating, and filtering off the manganese dioxide on an asbestos filter.

(11) Owing to the fact mentioned above that zinc is carried down in considerable quantity by manganese in the Na_2O_2 precipitation, experiments were made with the view of previously removing manganese by introducing this chloric acid procedure at the beginning of the analysis of this group. It was found, however, that vanadium, which is not carried down in the sodium peroxide procedure, is, like titanium, precipitated in large quantity with the manganese in the chloric acid procedure. It was found also that some zinc (1–4 mg.) may be carried down completely in the Na_2O_2 precipitate by iron, nickel and cobalt, so that it would be still necessary to provide for the detection of zinc in the iron group. For these reasons, it is evidently best to have the sodium peroxide precipitation precede the treatment with chloric acid.

(12) The filtrate from the chloric acid precipitate is first tested for phosphate. When it is not present, the iron, thallium, titanium and zirconium are separated from the other elements by the addition of ammonium hydroxide. When phosphate is present, in order to separate it from the alkaline-earth elements, the basic acetic precipitation is employed, ferric chloride being first added, if necessary. The provision here made for the case that phosphate is present is thought to have many advantages over the methods ordinarily employed in schemes of qualitative analysis, where the phosphate is removed by tin in nitric acid solution, by ferric chloride and barium carbonate, or by ferric chloride and ammonium acetate in the first stages of the analysis of the group. Of these three processes, the basic acetate is much more rapid and simple of execution; but it does not give a separation which is at all satisfactory when applied to a solution containing all the elements of the aluminum and iron groups; thus chromium and zinc may in certain combinations of elements be found either in the precipitate or filtrate, and manganese also divides, unless great care is taken to make the precipitation in a large volume at the proper acid concentration. In the scheme of analysis here presented, this basic acetate separation has been introduced only after these troublesome elements have already been removed, for the presence of phosphate involves no complications in the preceding steps of the process. Under these circumstances it is no more difficult to secure accurate results in this separation than in the precipitation with ammonium hydroxide. Indeed, by adopting this process for all cases the complication of the alternative procedure and the special test for phosphate might be removed; but since the operations require a somewhat longer time, it has seemed best to retain the

ammonium hydroxide precipitation for the case that phosphate is not present.

(13) The iron might be separated from the titanium and zirconium by the well-known method of boiling a solution of the elements kept slightly acid with sulphurous acid; but it is difficult to secure complete precipitation of the titanium and zirconium and at the same time to prevent the carrying down of iron. Besides this, the operation is a long one, involves large dilution, and makes it necessary to use hydrofluoric acid in redissolving the precipitated hydroxides. On the other hand, the removal of the iron by the method of Rothe,[1] which consists in shaking it out of a strong hydrochloric acid solution by means of ether, is extremely simple and rapid, gives a perfect separation, and leaves the titanium and zirconium in solution. We have therefore unhesitatingly employed this method in our scheme of analysis. Moreover, in this process the thallium, which is present as thallic chloride, is extracted together with the ferric chloride by the ether; it can be readily detected, after evaporating off the ether and reducing the ferric and thallic salts with sulphurous acid, by the formation with potassium iodide of the characteristic yellow precipitate of thallous iodide.

(14) For the separation of the titanium and zirconium from each other we have adopted the process of Hillebrand,[2] which consists in adding sodium phosphate to a slightly acid solution containing hydrogen peroxide, whereby the zirconium is precipitated and the titanium remains in solution. The latter is shown to be present by the color of the solution, but it can also be precipitated as phosphate by destroying the hydrogen peroxide with sulphurous acid after filtering off the zirconium compound.

(15) The analysis of the ammoniacal solution containing nickel, cobalt and perhaps zinc and the alkaline-earth elements, is carried out along the conventional lines. The first three elements are precipitated by the addition of ammonium sulphide, and the zinc is extracted, if the precipitate is large, by treating it with cold dilute hydrochloric acid, or if it is small by dissolving the precipitate completely and treating again with sodium peroxide. Instead of separating the nickel and cobalt from each other, it was found to be shorter and more conclusive to divide the solution of the sulphides into two parts and to test one portion for nickel by adding potassium cyanide and sodium hypobromite and the other portion for cobalt with potassium nitrite. The conditions for securing the best results in the nickel test were fully studied. Finally, in the filtrate from the ammonium sulphide pre-

[1] Rothe, Stahl und Eisen, 12, 1052 (1892), 13, 333 (1893).

[2] Bull. U. S. Geol. Survey, No. 176, p. 75 (1900).

cipitate the alkaline-earth elements are precipitated with ammonium carbonate as usual.

(16) Though no provision is made in the system of analysis for the separate detection of any of the rare-earth elements, yet a process has been described for determining whether any of them are present and for removing them when they are found to be in the solution. This process consists in evaporating the acid solution of the original ammonium sulphide precipitate, adding to the residue hydrofluoric acid and filtering. This converts the rare-earth elements completely into insoluble fluorides, and enables them to be separated from all the other elements of the aluminum and iron groups (except from a very large quantity of aluminum). When alkaline-earth elements are present, these are also precipitated as fluorides, wholly or in part, and are separated from the rare-earth elements by decomposing the fluorides with sulphuric acid, diluting, filtering off any alkaline earth sulphates that separate, and precipitating the rare-earths in the filtrate with ammonium hydroxide. This process of isolating the rare elements has been worked out in this laboratory by W. C. Arsem and H. I. Wood, for use as a group separation in the "System of Qualitative Analysis Including Nearly all the Metallic Elements."[1]

(17) Final confirmatory tests are given for almost all the elements; and much experimenting has been done on some of these tests in order to make them delicate and reliable; thus, this is true of the color tests for aluminum and zinc made by igniting the oxides with cobalt nitrate, of that for chromium with hydrogen peroxide and ether, of that for nickel with H_2S in an alkaline tartrate solution, and of that for vanadium made by adding H_2O_2 to an acid solution; also of the precipitation test for uranium with potassium ferrocyanide. No satisfactory tests have as yet been found for beryllium or zirconium. Many, but not all, of these confirmatory tests will be found superfluous and will be omitted by the experienced analyst, except in cases where a very small precipitate or one of doubtful character is obtained; but they will, we believe, be useful to those unfamiliar with this scheme, and they serve, in the case of students, the educational purpose of making them acquainted with additional reactions of the elements in question.

(18) It may be thought an objection to this scheme of analysis that it involves a number of manipulative operations unusual in qualitative analysis, such as heating in a closed bottle, saturating the acid-ether solution with hydrogen chloride gas (in the separation of aluminum and beryllium), filtering through an asbestos filter (in the separation of manganese), and shaking out with ether in the separation of iron from

[1] Two parts of this "System" have already been published. Technology Quarterly, 16, 93–131 (1903); 17, 214–257 (1904).

titanium and zirconium. These operations, when they have been once executed, are found to be little if any more troublesome than the ordinary operations of precipitation and filtration. They are, moreover, mostly employed only in connection with the detection of the rarer elements, where the difficulties in finding any satisfactory method are so great that a little additional trouble is an insignificant factor. And finally, from an educational standpoint, they introduce the student to new kinds of processes, thus enlarging his knowledge and diminishing the force of the objection that the ordinary study of qualitative analysis is too limited in its scope.

Tabular Outline.

In the tables below the enclosure of a symbol in brackets shows that the element may divide itself between the residue and the solution in the operation immediately preceding.

Procedure and Notes.

Procedure 51.—Boil the filtrate from the H_2S precipitate (P. 21)[1] till the H_2S is expelled. Transfer it to a flask, add NH_4OH (0.96) until the mixture after shaking smells of it, and then 2–4 cc. more. Note whether there is a precipitate. Add ammonium monosulphide slowly (or if nickel is likely to be present pass in H_2S), until, after shaking, the vapors in the flask blacken a piece of filter-paper moistened with lead acetate solution. To coagulate the precipitate shake the mixture or heat it nearly to boiling. Filter, and wash the precipitate, first with water containing about 1 per cent. of the $(NH_4)_2S$ reagent and then with a little pure water. If the filtration is slow, keep the funnel covered with a watch glass so as to prevent oxidation. To the filtrate add a few drops $(NH_4)_2S$, boil the mixture for a few seconds, or longer if it is dark colored (till it becomes colorless or light yellow); filter if there is a precipitate, uniting it with the preceding one. (Precipitate, P. 52; filtrate, P. 71, or first by *P. 51*a*, if vanadium is to be tested for.)

Notes.—(1) The H_2S is boiled out, and the effect of the addition of NH_4OH alone is noted because it often gives a useful indication as to what elements are present. To save time the expulsion of the H_2S may be omitted when this indication is considered unimportant. Ammonium monosulphide is used, rather than polysulphide, in order to prevent as far as possible the dissolving of NiS, and in order not to introduce sulphur into the precipitate, or polysulphide into the filtrate; for this gives to the filtrate a deep yellow color, and causes in the subsequent analysis separation of sulphur on standing or on heating. Excess of the monosulphide is avoided, for the same reasons, since it rapidly oxidizes in the air to polysulphide. By passing H_2S into the ammoniacal solution instead of adding $(NH_4)_2S$, the dissolving of NiS is entirely prevented; therefore, though the operation takes a little longer, the use of H_2S is to be preferred when nickel is likely to be present. The mixture is shaken in order

[1] For this and similar references to former procedures, see the previous article, THIS JOURNAL, 29, 137.

TABLE VII.

Analysis of the Aluminum and Iron Groups for Common Elements.

To the filtrate from the H_2S precipitate add NH_4OH and $(NH_4)_2S$ (P. 51).

- Precipitate: $Al(OH)_3$, $Cr(OH)_3$, ZnS, MnS, FeS, Fe_2S_3, NiS, CoS. *Dissolve in HCl or HCl + HNO_3, evaporate, add NaOH, Na_2O_2 and Na_2C*
  - Filtrate: $NaAlO_2$, Na_2CrO_4, Na_2ZnO_2. *Acidify with HNO_3, add NH_4OH (P. 53).*
    - Precipitate: $Al(OH)_3$. *Dissolve in HNO_3, add $Co(NO_3)_2$, evaporate, ignite (P. 54).*
      - Blue residue: $Al_2O_3.xCoO$.
    - Filtrate: *Add $HC_2H_3O_2$ and $BaCl_2$ (P. 55).*
      - Precipitate: $BaCrO_4$. *Dissolve in dilute HNO_3, add ether and H_2O_2 (P. 56).*
        - Blue coloration of ether layer: H_3CrO_7.
  - Precipitate: MnO(OH [ZnO_2H_2]. *Dissolve in HCl, evapo*
    - Precipitate: MnO_2. *Boil with HNO_3 and PbO_2 (P 62).*
      - Violet color: $HMnO_4$.
    - Precipitate: $Fe(OH)_3$. *Dissolve in HCl, add KSCN.*
      - Red solution: $Fe(SCN)_3$.
    - [illegible] (P. 57).
      - White precipitate: ZnS.
      - *Dissolve, evaporate, add NaOH.*
        - *To one-half* (P. 69). Yellow precipitate: $K_3Co(NO_2)_6$.
        - *To other half add KCN, digest, add NaBrO (P. 70).* Black precipitate: $Ni(OH)_3$.
    - White precipitate: ZnS. *Dissolve in HNO_3, add $Co(NO_3)_2$, ignite (P. 57).*
      - Green residue: ZnO,xCoO.
- Filtrate: Alkaline-earth and alkali elements.

[1] Test for phosphate at this point (P. 63); if present, follow Table IX.

TABLE VIII.

ANALYSIS OF THE ALUMINUM GROUP FOR COMMON AND RARE ELEMENTS.

Filtrate from Na_2O_2 treatment: Na_2CrO_4, sodium peruranate, Na_3VO_4, Na_2ZnO_2, $NaAlO_2$ Na_2BeO_2.
*Add HNO_3, dilute, add $NaHCO_3$, heat in a closed bottle (*P. 58a).*

- Filtrate: salts of chromic, uranic and vanadic acids. *Add HNO_3 and $Pb(NO_3)_2$ (*P. 58 b).*
  - Yellow precipitate: $PbCrO_4$.
  - Filtrate: $UO_2(NO_3)_2$, H_3VO_4, $[Pb(NO_3)_2]$. *Pass in H_2S.*
    - Precipitate: PbS. *Reject.*
    - Filtrate: *Add bromine, neutralize, add $HC_2H_3O_2$ and Na_2HPO_4 (*P. 58c).*
      - Precipitate: $UO_2NH_4PO_4$. *Dissolve in HCl, evaporate, add NaCl and $K_4Fe(CN)_6$. (*P. 58d).*
      - Brown precipitate: $(UO_2)_2Fe(CN)_6$.
- Precipitate: $ZnCO_3$, $Al(OH)_3$, basic $BeCO_3$. *Dissolve in HCl, add NH_4OH (*P. 58f).*
  - Filtrate: $Zn(NH_3)_4Cl_2$. *Add $HC_2H_3O_2$, pass in H_2S. (P. 57).*
  - Precipitate: $Al(OH)_3$, $Be(OH)_2$. *with HCl gas (*P. 58g).*
    - White precipi-
    - Filtrate: *Evaporate, add 10 per*

[1] Filter, and test the precipitate for uranium (*P. 58h).

TABLE IX.

ANALYSIS OF THE IRON GROUP FOR THE RARE ELEMENTS, AND FOR THE COMMON ELEMENTS IN THE PRESENCE OF PHOSPHATE.

Precipitate from Na_2O_2 treatment: $MnO(OH)_2$, $Fe(OH)_3$, $Tl(OH)_3$, $ZrO(OH)_2$, $TiO(OH)_2$, $Co(OH)_3$, $Ni(OH)_2$, $Ni(OH)_3$, [$Zn(OH)_2$]; $CaCO_3$, $SrCO_3$, $BaCO_3$, $MgCO_3$; and phosphates of these elements.

Dissolve in HCl, evaporate, heat with HNO_3 and $KClO_3$ (P. 61).

Brown precipitate: MnO_2.	

[1] Test for phosphate at this point (P. 63); if found absent, make the solution alkaline with NH_4OH (omitting the addition of ammonium acetate and $FeCl_3$), and filter.

to coagulate the precipitate, and make it filter more readily. Heating also promotes the coagulation of the precipitate, and it is recommended when the precipitate does not coagulate and settle quickly on shaking. The filtrate is boiled for a few moments to ensure the complete precipitation of $Cr(OH)_3$, or longer to ensure that of NiS, whose presence is indicated by a brown or nearly black color of the filtrate. Finally it is directed to wash with water containing a little $(NH_4)_2S$, and to keep the filter covered, in order to avoid the oxidation of the sulphides by the air, by which soluble sulphates may be formed.

(2) Under the conditions of the procedure, which provides for a small excess of NH_4OH in the presence of NH_4Cl, aluminum, chromium, iron, titanium, zirconium, and beryllium are completely precipitated as hydroxides and uranium as ammonium diuranate, $(NH_4)_2U_2O_7$. All of these precipitates are white, except those of chromium, uranium, and iron; $Cr(OH)_3$ is grayish-green, and $(NH_4)_2U_2O_7$ is yellow. The color of the precipitated hydroxide of iron varies with the state of oxidation of the iron, pure ferrous salts yielding a white precipitate, and ferric salts a reddish-brown one, while mixtures of them yield green or black precipitates. In the alkaline mixtures the precipitate is rapidly oxidized by the oxygen of the air and undergoes corresponding changes in color. Manganous salts are also oxidized rapidly, with the result that brown $Mn(OH)_3$ separates. Under the conditions of the procedure zinc and nickel when present alone, are completely dissolved; the same is true of cobalt except when it is present in large quantity; but zinc is precipitated when chromium is also present. The ammoniacal solution of nickel is blue and that of cobalt of a reddish color, which darkens rapidly on exposure to the air owing to oxidation. If a smaller excess of NH_4OH is used than is directed, some zinc hydroxide, as well as cobalt hydroxide, may remain undissolved when large amounts of these elements are present; but this has no effect on the subsequent analysis. If, however, a much larger excess of NH_4OH is employed, a few milligrams of aluminum and chromium may be dissolved, the latter giving a pink colored solution.

(3) The presence of a considerable quantity of NH_4Cl, such as is formed by the neutralization of the acid already in the solution, serves to prevent the precipitation of $Mg(OH)_2$ (and of $Mn(OH)_2$), and also to lessen the amount of $Al(OH)_3$ dissolved by the NH_4OH.

(4) The influence of an excess of the NH_4OH and of the presence of NH_4Cl on the solubilities of the various hydroxides is explained by the mass-action law and ionic theory as follows: In order that any hydroxide, say of the type MO_2H_2, may be precipitated, it is necessary that the product $C_M.C^2_{OH}$ of the concentrations of the ions M^{++} and OH^- in the solution in question attain the value known as the solubility-product. This varies, of course, with the nature of the hydroxide; but for all the elements of the iron group and also for magnesium it has so small a value that, even in a solution containing in 50 cc. only one milligram of the element and a slight excess of NH_4OH, the product $C_MC^2_{OH}$ exceeds it, and precipitation results. When, however, much NH_4Cl is also present, this greatly reduces, in virtue of the common ion effect, the ionization of the NH_4OH and therefore the OH^- concentration in the solution, so that now for certain elements the product $C_MC^2_{OH}$ does not reach the solubility value, even when C_M is moderately large (say 500 mg. in 50 cc.). This is true of magnesium and manganese; but in the cases of aluminum, chromium, and ferric iron the solubility of the hydroxides in water is so slight that even in NH_4Cl solution the solubility is not appreciable.

If these were the only effects involved, the greater the excess of NH_4OH added, the less would be the solubility of any hydroxide; but other influences come into play with certain of the elements. These influences are of two kinds. The first of these

is shown by zinc, nickel, and cobalt. In the case of these elements, just as with silver and copper, the excess of ammonia combines with the simple cathion M^{++} forming complex cathions of the types $M(NH_3)_2^{++}$ and $M(NH_3)_4^{++}$, thereby removing the simple cathion from the solution and making it necessary for more of the hydroxide to dissolve, in order to bring back the value of $C_M C^2_{OH}$ to that of the solubility-product. In such a case, the presence of NH_4Cl increases the solubility still further, since it greatly decreases C_{OH} and slightly increases C_{NH_4OH} and C_{NH_3}, owing to the common ion effect on the ionization of the NH_4OH. Chromium also forms similar ammonia complexes, but in much smaller proportion.

The second effect is exhibited in the case of AlO_3H_3. This hydroxide is a so-called amphoteric substance,—*i. e.*, is one which behaves both as a base and as an acid in consequence of its being appreciably ionized both into $3(OH^-) + Al^{+++}$ and into $H^+ + AlO_3H_2^-$ (or AlO_2^- and H_2O). With the H arising from the latter form of ionization, the OH^- coming from the excess of NH_4OH combines to form H_2O thus causing more AlO_3H_3 to dissolve until the value of $C_{AlO_2^-} \cdot C_H$ again attains that of the solubility-product. Since $C_{AlO_2^-} \cdot C_H =$ const. in any solution saturated with AlO_3H_3 and since the equilibrium equations $C_H \cdot C_{OH} = K_W$ and $C_{NH_4} C_{OH} = K_2 C_{NH_4OH}$ must be satisfied, it follows from combination of these equations that $C_{AlO_2^-}/C_{OH} =$ const. and that $C_{AlO_2^-} =$ const. $\times C_{NH_4OH}/C_{NH_4}$. The first equation shows that the quantity of aluminum dissolved is proportional to the concentration of hydroxide-ion in the solution, and that therefore it would be much greater in a solution of a largely ionized base like NaOH than in that of a slightly ionized base like NH_4OH. The second equation shows that the solubility in solutions containing NH_4OH and NH_4Cl (or other ammonium salt) is proportional to the ratio of the concentration of the base to that of the salt; so that the presence of ammonium salts tends to neutralize the solvent action of an excess of the hydroxide. All these conclusions are in accordance with the facts. BeO_2H_2 behaves in the same way as AlO_3H_3, forming the cation Be^{++} and the anion $BeO_2^=$ or $HBeO_2^-$.

(5) It follows from the statements in the preceding notes that if the NH_4OH produces no precipitate it proves the absence of as much as one milligram of aluminum, iron, beryllium, uranium, titanium, and zirconium; also of chromium, if the mixture is heated to boiling after the addition of NH_4OH. Care must be taken not to overlook a small precipitate which might otherwise escape detection on account of its transparency. The mixture should therefore be well-shaken and allowed to stand 2 or 3 minutes in order that the precipitate may collect in flocks. This treatment also oxidizes the iron when present in small quantity, and thus enables it to be more readily detected; for its precipitation in the ferric state is more complete.

(6) When phosphate is present, magnesium, calcium, strontium, barium, and manganese may be partially, or even completely precipitated by NH_4OH. It is therefore necessary, when phosphate is present, to provide for the detection of the alkaline earth elements in the analysis of this precipitate. The normal phosphates and the monohydrogen phosphates of these elements are difficultly soluble in water, but dissolve readily in acids, owing to the formation in solution of the much more soluble dihydrogen phosphates or of free phosphoric acid, for example, according to the equations:

$$(Ca^{++})_3(PO_4^{\equiv})_2 + 4H^+Cl^- = 2Ca^{++}(Cl^-)_2 + Ca^{++}(H_2PO_4^-)_2$$
$$Ca^{++}(H_2PO_4^-)_2 + 2H^+Cl^- = Ca^{++}(Cl^-)_2 + H_3PO_4.$$

Upon the addition of sodium or ammonium hydroxide to such a solution the hydrogen-ion in equilibrium with the $H_2PO_4^-$ and H_3PO_4 is removed, and these dissociate into $HPO_4^=$ and $PO_4^{\equiv}$, thus causing precipitation of the corresponding salts. When other elements, like iron, forming more insoluble phosphates are also present, it is evident

that they will combine with the phosphate radical, thus leaving the alkaline earth elements in solution. On the other hand, when a soluble carbonate, or a large excess of a strong base, is also present, the alkaline earth phosphates will be partially converted into carbonates or hydroxides, leaving phosphate in solution.

(7) The presence of any other acid radical which forms with the alkaline earth elements salts soluble in dilute acids but insoluble in ammonia may also cause their precipitation at this point. Such radicals are fluoride, borate, oxalate, and hypovanadate. The fluoride will ordinarily have been removed in the evaporation with acids in the preparation of the solution. The borates of the alkaline earth elements, though somewhat difficultly soluble, are not sufficiently so to cause them to be precipitated, except when present in very large quantity. Oxalate and hypovanadate, even if present, do not make any change necessary in the usual process of analysis; for, in the course of it, vanadate and much of the oxalate are separated from the alkaline earths in P. 52, and the remainder of the oxalate is destroyed in P. 61.

(*8) Vanadium when present alone in moderate quantity may remain in solution, but when present in large quantity is partially precipitated by NH_4OH as a dark gray hydroxide, $VO(OH)_2$. This compound corresponds to the state of oxidation (oxide VO_2) to which vanadic acid (oxide V_2O_5) is partially or completely reduced by H_2S. It is an amphoteric substance which forms with acids soluble blue salts such as $VOCl_2$, vanadyl dichloride, and $VOSO_4$, vanadyl sulphate, and with bases hypovanadates such as $Na_2V_2O_5$ and $Na_2V_4O_7$. When other elements of this group are also present the vanadium may be completely precipitated with them, since their hypovanadates and vanadates are in general difficultly soluble substances.

(*9) When a base is added to a uranyl salt (for example UO_2Cl_2), uranyl hydroxide, $UO_2(OH)_2$, is first formed, but this is an amphoteric substance, and it is converted by the excess of base into salts of diuranic acid, $H_2U_2O_7$, of which even the alkali salts are insoluble.

(10) $(NH_4)_2S$ precipitates ZnS, MnS, NiS, CoS, and Tl_2S, and converts $Fe(OH)_2$ into FeS, $Fe(OH)_3$ into Fe_2S_3, and $(NH_4)_2U_2O_7$ very slowly into UO_2S. The hydroxides of aluminum, chromium, titanium, zirconium, and beryllium are not affected by the $(NH_4)_2S$. Whether a hydroxide precipitate is converted into a sulphide precipitate or whether the reverse reaction takes place depends on the relative solubilities of the two compounds and on the relative concentrations of sulphide-ion and hydroxide-ion in the solution. Since in the solution the concentration of the sulphide-ion greatly exceeds that of the hydroxide-ion, even difficultly soluble hydroxides would be converted into more soluble sulphides, provided that the difference in solubility were not too great. In the case of hydroxides, like $Al(OH)_3$, which are not so changed, their sulphides are so much more soluble that they do not form in aqueous sulphide solutions.

(11) The sulphides of iron, nickel, and cobalt are black; Tl_2S and UO_2S are dark brown; ZnS is white; and MnS is flesh colored, but turns brown on standing in the air owing to oxidation to hydrated Mn_2O_3.

(12) When nickel is present alone, or in large proportion in the $(NH_4)_2S$ precipitate, several milligrams of it usually pass into the filtrate making it dark colored, and some NiS also passes through the filter with the wash water. In this case it is useless to try to remove the NiS by filtering again; but it can be coagulated by boiling for several minutes. This behavior of nickel, as stated above, can be avoided altogether by passing H_2S into the NH_4OH solution to precipitate the sulphide, instead of adding $(NH_4)_2S$. The formation of this brown solution depends upon the presence of ammonium polysulphide, for nickel may be completely precipitated by

ammonium monosulphide in the absence of air. The nature of the brown solution is not known.

***Procedure 51a.**—To the filtrate from the $(NH_4)_2S$ precipitate (P. 51) add 5 cc. NH_4OH (0.90) and completely saturate the solution with H_2S. (Pink or violet-red color, presence of *vanadium.*)

If no red color results, boil the solution for several minutes in a casserole to expel most of the NH_4OH and $(NH_4)_2S$, filter off the sulphur, and treat the filtrate by P. 71.

If the solution assumed a pink or red color, acidify it with HCl (1.12), heat it to boiling, and filter. Boil the filtrate in a casserole to expel H_2S, add 0.5–5 cc. 10 per cent. $FeCl_3$ solution, and NH_4OH (0.96) until the mixture after shaking smells of it, and filter. (Filtrate, P. 71.) Heat the HCl precipitate (with the filter, if necessary) with 5–10 cc. HNO_3 (1.20) until the black precipitate is dissolved, and filter. (If the red coloration produced by H_2S was slight, evaporate the filtrate to about 2 cc.) Add to the solution a few drops of 3 per cent. H_2O_2. (Orange-yellow or orange-red color, presence of *vanadium.*) Dissolve the NH_4OH precipitate by pouring a small portion of HNO_3 (1.20) repeatedly through the filter, and test for vanadium with H_2O_2 in the same way, first adding a little water to the HNO_3 solution if it has a red color owing to the presence of much ferric nitrate.

Notes.—(1) An ammoniacal solution of a vanadate or hypovanadate quickly becomes yellowish red when H_2S is led into it, and this color slowly deepens as more H_2S is absorbed; but the characteristic, brilliant violet-red color is obtained only when the solution is completely saturated with H_2S. The presence of ammonium salts tends to prevent the formation of this red compound, but their influence is overcome by the addition of a large excess of NH_4OH. These facts make it probable that this red compound is an ammonium sulpho vanadate, from which the sulphur is readily split off as SH^- ion, owing to hydrolysis. Under the conditions of procedure, 0.2 mg. V can be easily detected, the solution then having a pink color.

(2) Upon the addition of HCl the sulpho salt is immediately decomposed, with formation of a black precipitate of V_2S_4 or V_2S_5. This precipitation is far from complete under these conditions, only about half the vanadium being thrown down. More or less sulphur will also be precipitated, but the dark color of the sulphide is apparent even when less than 0.5 mg. V is present. Acetic acid may be used instead of HCl, but the proportion of vanadium precipitated as sulphide is not much increased.

(3) When a three- to fivefold excess of a ferric salt is present and NH_4OH is added, the remainder of the vanadium is precipitated (probably as hypovanadate) together with the $Fe(OH)_3$.

(4) The confirmatory test for vanadium with H_2O_2 depends upon the formation of pervanadic acid, HVO_4. 0.1 to 0.2 mg. V may be detected in a volume of 5 cc., provided that this solution is strongly acid. A very large excess of H_2O_2 is to be avoided, for this decreases the intensity of the color, and may even decolorize the solution completely if very little acid is present, probably owing to the formation of a colorless compound of pervanadic acid with hydrogen peroxide.

(5) Molybdenum, if not completely precipitated by H_2S in P. 21, and tungsten, if it passed into the original acid solution (owing to the presence of phosphate or ar-

senate) in P. 3, may also be present in the filtrate from the $(NH_4)_2S$ precipitate. Upon saturating with H_2S molybdenum also gives a deep red color which would obscure the test for vanadium and might be mistaken for it; but tungsten gives no color. Upon acidification with HCl, tungsten divides between the pecipitate and filtrate, but molybdenum is thrown down completely as black MoS_3. (If the cold solution is acidified with acetic acid, the sulphomolybdate remains undecomposed for some time and the MoS_3 is not completely precipitated even on boiling.) In the final confirmatory test with H_2O_2 tungsten gives no color; and molybdenum, even when a large quantity is present, gives only a pure yellow color but not an orange or red one.

Procedure 52.—Transfer the $(NH_4)_2S$ precipitate (P. 51) with the filter if necessary to a casserole; add 5–20 cc. HCl (1.12), stir for a minute or two in the cold, and then boil the mixture for two or three minutes; if a black residue still remains, add a few drops HNO_3 (1.42) and boil again. Dilute with a little water, filter off the sulphur residue, and evaporate the filtrate to a small volume to remove the excess of acid.

*In order to detect rare earth elements, and to remove them if present, treat this solution by *P. 52*a*.

*If uranium and vanadium are to be tested for later by *P. 58*a–h*, evaporate twice with a little HNO_3 (1.42), to destroy HCl.

Dilute the solution to 10 or 20 cc.; make alkaline with NaOH solution, avoiding a great excess; add 10–20 cc. more water if so large a precipitate separates that the mixture becomes almost gelatinous. Cool by placing the casserole in cold water, and add 0.5–3 gram solid Na_2O_2, in small portions with constant stirring. Then add 5 cc. 10 per cent. Na_2CO_3 solution; boil for two or three minutes to decompose the excess of Na_2O_2, cool, dilute with an equal volume of water, filter with the help of suction and wash with hot water. (Precipitate, P. 61; filtrate, P. 53, or if uranium or vanadium is to be tested for, *P. 58*a*.)

Notes.—(1) All the hydroxides and all the sulphides, except NiS, CoS, usually dissolve readily in cold HCl. If, therefore, there is considerable black residue after adding the HCl, it shows the presence of nickel, or cobalt (or possibly vanadium); a very small black residue may, however, be due to FeS enclosed within sulphur. The fact that there is no such dark colored residue does not, however, prove that nickel and cobalt are absent, for a considerable quantity of them (even 5 mg.) may dissolve completely in the HCl when large quantities of other elements, especially iron, are also present.

(2) The fact that NiS and CoS dissolve so much less readily in dilute acids than do the other sulphides of this group seems to be due not to a lesser solubility in water, but to an unusually slow rate of solution, for nickel and cobalt are not precipitated by H_2S even from a much more weakly acid solution, and their sulphides obtained by precipitation with an alkaline sulphide continue to dissolve in dilute acids without reaching a limit determined by the concentration of the H_2S and the nickel-ion or cobalt-ion in the solution, as would be the case if the phenomena were that of the solubility of a difficultly soluble sulphide.

(3) The $(NH_4)_2S$ precipitate is first treated with HCl, partly in order to furnish the indication just referred to of the presence of nickel or cobalt but mainly because much more free sulphide and sulphate would be formed by oxidation if HNO_3 or *aqua*

regia were used at the start. The presence of the sulphate in considerable quantity in the solution interferes with the subsequent test for chromate (with $Ba(NO_3)_2$ in P. 55 or with $Pb(NO_3)_2$ in *P. 58*b*). If NiS, CoS, or V_2S_5 is present in the residue, HNO_3 must, however, be subsequently added, to ensure the solution of these sulphides. *The HCl is destroyed by evaporation with HNO_3, since chloride interferes with the test for chromate with $Pb(NO_3)_2$ in *P. 58*b*.

(*4) If the $(NH_4)_2S$ precipitate be allowed to stand for a long time before treating it with acid, or if the mixture be heated for a long time after the precipitation, $TiO(OH)_2$ and $ZrO(OH)_2$ may remain in part undissolved even by the boiling concentrated acids, owing to the fact that the hydroxides at first precipitated become partially dehydrated, in which state they are very difficultly soluble. If this happens at this point or in dissolving hydroxide precipitates obtained later in the analysis, the residue may be dissolved in a little HF in a platinum dish, and the HF then expelled by evaporating two or three times with HNO_3 (or HCl) nearly to dryness.

(5) By NaOH, iron, manganese, nickel, cobalt, *titanium, *zirconium, and *uranium are completely precipitated and do not dissolve in moderate excess; while aluminum, chromium, zinc, *vanadium, and *beryllium, remain in solution or dissolve when a sufficient excess is added, owing to the fact that their hydroxides are amphoteric substances (see P. 51, Note 3), and form with the NaOH soluble aluminate ($NaAlO_2$), chromite ($NaCrO_2$), zincate (Na_2ZnO_2), vanadate (Na_3VO_4), and beryllate (Na_2BeO_2). Thallium in the thallous state also remains in solution since TlOH is a readily soluble substance. When zinc and chromium are simultaneously present, they are precipitated in the form of a double compound ($ZnCr_2O_4$). Chromium would also be completely precipitated, owing to hydrolysis and the formation of a less soluble solid hydroxide, if the NaOH solution were boiled before adding Na_2O_2. It will be observed that NaOH precipitates manganese, nickel and cobalt while NH_4OH does not. This occurs with manganese because of the far greater concentration of hydroxide-ion in the NaOH solution, and with nickel and cobalt partly on this account and partly because there is no complex formation, as there is with NH_4OH. $Mn(OH)_2$ is white, but rapidly turns brown, owing to oxidation to $Mn(OH)_3$; $Ni(OH)_2$ is light green; $Co(OH)_2$ is pink, but from cobalt solutions a blue basic salt is first precipitated in the cold. If a large excess of NaOH be added, a little $Co(OH)_2$ dissolves yielding a blue solution, doubtless forming a salt such as Na_2CoO_2. This is to be avoided since then the cobalt will not be completely oxidized and precipitated upon the subsequent addition of Na_2O_2.

(6) By the addition of Na_2O_2, $Fe(OH)_2$ is changed to dark red $Fe(OH)_3$, $Mn(OH)_2$ to brown hydrated MnO_2, $Co(OH)_2$ to black $Co(OH)_3$, $Ni(OH)_2$ partially to black $Ni(OH)_3$, and thallium is precipitated as dark red $Tl(OH)_3$, all of which are insoluble in excess of NaOH and remain, together with $TiO(OH)_2$ and $ZrO(OH)_2$, in the precipitate. Chromium and uranium, which after the addition of NaOH are present as soluble sodium chromite or as insoluble sodium diuranate ($Na_2U_2O_7$), are converted by Na_2O_2 into chromate (Na_2CrO_4) and peruranate which are soluble compounds and remain in solution, together with the zinc, beryllium, and vanadium, which are still present as zincate, beryllate, and vanadate. The separation is more satisfactory, especially in the case of uranium when a large amount Na_2O_2 is used

(7) Even a cold solution of Na_2O_2 decomposes rapidly with evolution of oxygen, and this decomposition takes place with explosive violence when the solution is hot. The peroxide is therefore added in small portions to the cold solution. A steady evolution of gas continuing after the mixture has been well-stirred is an indication that sufficient peroxide has been added. The mixture is finally boiled in order to destroy the excess of Na_2O_2 and to cause the complete precipitation of titanium, some

of which first passes into solution, probably as the pertitanate. The solution is cooled because $Tl(OH)_3$ is somewhat more soluble in the hot solution than in the cold one. Even in the cold when thallium is present alone about 0.5 mg. will usually pass into the filtrate but precipitation is complete when elements of the iron group are also present. The solution is diluted before filtering in order to avoid the disintegration of the filter paper; it is often advantageous to support the filter by folding it together with a small hardened filter.

(8) The Na_2CO_3 is added to cause the complete precipitation of the alkaline-earth elements, whose hydroxides, especially that of barium, are somewhat soluble even in the presence of NaOH. $ZnCO_3$, though insoluble in a dilute solution of Na_2CO_3 alone, dissolves when much NaOH is present, owing to the nearly complete conversion of the zinc-ion into zincate-ion by the reaction $Zn^{++} + 4OH^{-} = ZnO_2^{=} + 2H_2O$. The Na_2CO_3 also serves to decompose the chromates of the alkaline-earth elements; if it is not added, chromium may remain in the precipitate and escape detection. It is unnecessary to add the Na_2CO_3 when the alkaline-earth elements are known to be absent.

(9) Phosphate or oxalate, if present, divides itself in this procedure between the precipitate and solution in a proportion which depends on the nature and quantities of the metallic elements. (See P. 51, N. 6.) Their presence does not cause any of the elements to precipitate which would not otherwise do so, in spite of the slight solubility of aluminum, zinc, and beryllium phosphates. This is due to the fact that the cathions of these elements (Al^{+++}, Zn^{++}, Be^{++}) are present in the NaOH solution only at an extremely small concentration, owing to their combination with the OH ion to form anions (AlO_2^{-}, $ZnO_2^{=}$, $BeO_2^{=}$).

(10) Even when less than 1 mg. Cr is present as chromate, it imparts a distinct yellow color to the alkaline solution, so that when a colorless solution results, it proves the absence of this element. Uranium in small quantity also gives a yellow color to the solution, which is noticeable with 1 or 2 mg.; a moderate amount (about 10 mg.) gives a red color, which is intense with still larger quantities. Alkaline solutions containing vanadium are colorless after boiling.

(11) This separation with NaOH, Na_2O_2, and Na_2CO_3 is a very satisfactory one, except in the case of zinc. This element, when present in small quantities, is completely carried down in the precipitate when much iron, nickel, or cobalt, or especially manganese, is present. Provision for the detection of zinc in the precipitate must therefore be made.

(12) If Na_2O_2 is not available, sodium hypobromite, NaBrO (prepared by mixing NaOH and bromine, as described in P. 70 N. 3), may be used as the oxidizing agent, but it is not quite so satisfactory as Na_2O_2, for it does not oxidize $Cr(OH)_3$ so readily, and it is apt to oxidize some of the manganese to $NaMnO_4$ (especially if there is not a sufficient excess of NaOH present).

***Procedure 52a.**—To detect rare earth elements, and to remove them, if present, transfer the acid solution (P. 52) to a platinum dish (after destroying HNO_3, if any has been added, by evaporating in porcelain once or twice with HCl (1.20)), and evaporate just to dryness. Add to the residue 45 per cent. HF solution, little by little, until the residue has been dissolved, or until about 25 cc. have been added, stirring with a platinum rod after each addition, and finally boiling gently under a hood for a minute or two if there is still a residue. Collect the residue on a filter supported on a platinum ring or in a celluloid

funnel; collect the filtrate in a platinum dish; wash the residue thoroughly with water.

To the filtrate add 3–5 cc. HCl (1.20), and evaporate it just to dryness; add a little HCl and evaporate again, and repeat these operations a third time. Dissolve the residue in a little water, adding HCl if necessary; transfer to a casserole, and treat the solution by the last paragraph of P. 52, first evaporating with HNO_3 to destroy HCl if chromium, uranium and vanadium are to be tested for by *P. 58*a–e*.

Transfer the residue insoluble in HF to a platinum crucible; if the filter has been added, ignite to destroy it. Add 2–5 cc. H_2SO_4 (1.20), heat until sulphuric acid fumes are given off, cool, add 10–20 cc. water, heat and filter. Treat the precipitate (which can consist only of $CaSO_4$, $SrSO_4$ or $BaSO_4$) with concentrated Na_2CO_3 solution by P. 6. To the H_2SO_4 solution add ammonia until alkaline. (White precipitate, presence of *rare earth elements*.) Filter and test the filtrate for calcium and magnesium. Wash the precipitate thoroughly, dissolve it in a little HCl, evaporate just to dryness in a platinum dish, dissolve in a little water, and add 5–10 cc. HF. (White precipitate, presence of *rare-earth elements*.)

Notes.—(1) Among the so-called rare earth elements are included thorium, cerium, lanthanum, praesodymium, neodymium, yttrium, ytterbium, and a number of other similar elements. These elements, like the alkali earth elements, are characterized by the insolubility of their fluorides; but differ from the alkali earth elements in that their hydroxides are precipitated by ammonia, and that their sulphates are not precipitated by sulphuric acid. It is upon these facts that the separation described in the above procedure is based. If there is no residue after the treatment with HF, it shows of course that the rare earth elements are absent; if, on the other hand, there is a residue, it does not necessarily show their presence, except when it is known that alkaline earth elements cannot be present. (See P. 51, N. 6 and 7.) The further treatment described in the procedure serves to eliminate the latter.

(2) Owing to the fact that aluminum and chromium fluorides are somewhat difficultly soluble in HF, care must be taken to use a rather large quantity of this acid when a residue remains. It is also obvious that the fluoride residue must be thoroughly washed, if the formation of a precipitate with ammonia is to be considered a conclusive indication of rare earth elements. The final treatment of the NH_4OH precipitate is recommended to eliminate the possibility of error from these sources.

(3) The HF solution, which may contain all the elements of the aluminum and iron groups, is evaporated repeatedly with HCl to expel the HF, which is especially apt to be retained when titanium and zirconium are present.

The Aluminum Group.

Procedure 53.—Acidify the alkaline solution (P. 52) with HNO_3 (1.42), avoiding a large excess; add NH_4OH (0.96) until the mixture after shaking smells of it, and then add 2–3 cc. more. Heat almost to boiling in order to coagulate the precipitate, filter, and wash thoroughly with hot water. (White, flocculent precipitate, presence of *aluminum*

(or **beryllium*); colorless solution, absence of *chromium*.) (Precipitate, P. 54, or to detect beryllium, *P. 58*g* and *h*; filtrate, P. 55.)

Notes.—(1) The alkaline solution is acidified with HNO_3, instead of with HCl, because the latter acid might reduce chromic acid, especially if a large quantity were added, or if the acid solution were heated. A moderate excess of NH_4OH must be added in order to keep the zinc in solution, which it does because of the production of $Zn(NH_3)_4^{++}(NO_3^{-})_2$; but a large excess is to be avoided, since it dissolves $Al(OH)_3$, owing to formation of $NH_4^{+}AlO_2^{-}$. The zinc is dissolved even when carbonate, phosphate, or oxalate is present.

(2) Since aluminum and silica are very likely to be present in the NaOH and Na_2O_2 used as reagents, and since they may be taken up from the dishes, a blank test for these impurities should be made whenever new reagents are employed for the first time, by following P. 52 and 53 and comparing the NH_4OH precipitate with that obtained in any regular analysis. It is also well at the same time to test for zinc by acidifying the NH_4OH solution with acetic acid and following P. 57.

Procedure 54.—Dissolve the precipitate (P. 53), or a small portion of it if it is large, in 5 cc. HNO_3 (1.20). From the appearance of the precipitate estimate the number of milligrams of aluminum which have been dissolved, and to the solution add about one-fourth as much cobalt as cobalt nitrate, using, however, not less than 0.2 mg. Evaporate almost to dryness in a casserole, add a drop or two of water, and soak up the solution in a small piece of filter-paper. Make a small roll of the paper, wind a platinum wire around it to form a spiral, and incinerate the paper in a small flame, finally heating the residue strongly. (Blue residue, presence of *aluminum*.)

Notes.—(1) This confirmatory test for aluminum should always be tried when the NH_4OH precipitate is small, for general reasons, inasmuch as the precipitation by NH_4OH of an element whose hydroxide is soluble in NaOH is not very characteristic (lead, antimony, tin, and beryllium showing a similar behavior), but also especially to guard against mistaking SiO_2H_2 for $Al(OH)_3$, for the former substance, if not entirely removed by proper dehydration in the process of the preparation of the solution (in P. 3, Part I), will appear at this point. A gelatinous precipitate which does not dissolve in HNO_3 indicates silica; it may be tested for by P. 5.

(2) The test described in this procedure depends upon the formation of a blue compound, whose formula is not definitely known; but it is doubtless a compound of the two oxides $CoO.xAl_2O_3$, and may be simply cobalt aluminate, $Co(AlO_2)_2$. It may be formed in various ways; but the process described in the procedure seems to be the most suitable one for making the test for aluminum reliable and delicate. It is of the utmost importance to have the aluminum present in excess; for, otherwise, the blue color is obscured by the black oxide of cobalt. In order that a small enough amount of cobalt may be added, it is convenient to use a very dilute solution of cobalt nitrate, say one that contains one-tenth of a milligram of cobalt per cubic centimeter.

(3) When the test is properly made, the ash retains the form in which the filter paper was rolled, and the whole mass, or a large part of it is colored blue. The presence of an equivalent amount of phosphate does not spoil the test. When sodium or potassium salts are also present, the ash fuses together, and the test is very unsatisfactory. For this reason the sodium salts present should be all washed out of the NH_4OH precipitate before dissolving it in HNO_3. No other element gives a blue color

to the ash, but certain elements, especially iron, obscure the test, so that it can be applied only after other elements have been removed in the regular process of analysis. 0.5 mg. Al may be easily detected, and even 0.2 mg. after a little practice.

(4) Another very good confirmatory test for aluminum consists in dissolving the NH_4OH precipitate in HCl (1.12), adding one and one-half volumes of ether, and saturating the mixture in the cold with HCl gas, as described in *P. 58 g. Under these conditions aluminum separates in the form of the crystalline compound $AlCl_3.6H_2O$; but no other element of the aluminum group is precipitated, except chromium, which if present in quantity greater than 10–20 mg. gives a violet precipitate. Moreover, silica does not interfere with this test. By this process, moreover, beryllium is quantitatively separated from aluminum, and may be tested for in the filtrate.

Procedure 55.—Acidify the NH_4OH solution (P. 53) with 30 per cent. acetic acid solution, avoiding an excess of more than 2 cc.

If the solution is colorless, treat it by P. 57.

If it is at all yellow, add about 10 cc. 10 per cent. $BaCl_2$ solution, allow the mixture to stand for at least five minutes and filter. (Yellow precipitate, presence of *chromium.*) (Precipitate, P. 56; filtrate, P. 57.)

Notes.—(1) The presence of less than 0.5 mg. chromium as chromate in a volume of 50 cc. makes the solution distinctly yellow, and the addition of $BaCl_2$ is therefore unnecessary when the solution is perfectly colorless. It is to be avoided, since $BaSO_4$ may be precipitated and has then to be removed by filtration. In doubtful cases the color of the solution should be compared with that of water. The color test is, of course, not delicate by artificial light.

(2) Since some sulphate may be present, the formation of a white precipitate with $BaCl_2$ does not prove the presence of chromium. Whether the precipitate is pure white or yellow should therefore be carefully noted. The yellow color of a small $BaCrO_4$ precipitate is most apparent when the precipitate has settled or when it has been collected on the filter. If there be sufficient sulphate present to obscure the yellow color of a little $BaCrO_4$, the confirmatory test for chromium described in the next procedure should be tried.

Procedure 56.—Pour repeatedly through the filter a 5–10 cc. portion of a mixture of 1 volume of HNO_3 (1.20) with 9 volumes of water; to the cold solution in a test-tube add about 2 cc. of ether and 1 cc. 3 per cent. H_2O_2, and shake. (Blue coloration of ether layer, presence of *chromium.*)

Notes.—(1) This blue compound which is formed by the action of H_2O_2 on chromic acid is one of the perchromic acids. It has the formula H_3CrO_7, and appears to be an addition product of H_2O_2 and a higher oxide of chromium. It is a very unstable substance; by its decomposition oxygen is evolved and the chromium is reduced to a chromic salt. Its decomposition is greatly accelerated by an excess of H_2O_2, by the presence of much acid, and by raising the temperature. It is therefore important not to add too much H_2O_2, and to use dilute acid, as directed in the procedure. If, in dissolving the precipitate, the filter be heated with HNO_3, the paper causes the chromate to be reduced to a chromic salt; but when the cold acid is merely poured through the filter this reduction does not take place. If a green solution should be obtained, the chromium must be reoxidized with Na_2O_2 in alkaline solution before

making the test. Under proper conditions 0.2 mg. Cr may be detected, but the test may fail with a much larger amount if the directions are not followed.

Procedure 57.—Warm the acetic acid solution (P. 55 or *P. 58*f*) to 50° or 60°, saturate it in a small flask with H_2S, cork the flask and allow it to stand for five or ten minutes if no precipitate separates at once. (White flocculent precipitate, presence of *zinc*.) Filter through a double filter (two filters folded together), wash once with a little water. Reject the filtrate.

To confirm the presence of zinc, pour a 5–10 cc. portion of HNO_3 (1.20) two or three times through the filter containing the H_2S precipitate. To the solution add an amount of cobalt as cobalt nitrate equal to about one-fourth of the amount of zinc estimated to be present, using, however, not less than 0.2 mg. cobalt. Evaporate in a casserole almost to dryness to expel the acid, neutralize with 10 per cent. Na_2CO_3 solution, and add about 0.5 cc. in excess. Evaporate to dryness, ignite gently until the purple color due to the cobalt disappears, and allow the casserole to cool. (Green color, presence of *zinc*.)

Notes.—(1) ZnS precipitates more rapidly, and in a somewhat more flocculent form, from a warm solution. Very small quantities of zinc (less than 1 mg.) may be missed unless a short time be allowed for the precipitate to coagulate; but, since sulphur may then separate, the appearance of a white turbidity is not sufficient proof of the presence of zinc. The precipitate may be allowed to settle, in order that the amount of zinc present may be better estimated. A double filter is used, since the ZnS is apt to pass through the filter.

(2) The immediate formation of a white flocculent precipitate with H_2S in acetic acid solution is so characteristic as to be a sufficient test for zinc. Manganese is the only other element of this group that forms a light colored sulphide; and this, owing to its greater solubility in water, does not precipitate from an acetic acid solution. The confirmatory test described in the last paragraph of the procedure is, however, useful when only a small non-coagulating precipitate, which may be sulphur, results, or when owing to the presence of a small quantity of other elements the precipitate is dark colored.

(3) The green compound obtained in the confirmatory test is doubtless a compound of cobalt and zinc oxides, perhaps cobalt zincate $CoZnO_2$. The conditions under which the zinc and aluminum compounds of cobalt are formed are very different. As we have seen, the aluminum compound is formed only at very high temperatures, and the test is not at all delicate in the presence of a salt of an alkali-element. On the other hand, the zinc compound is obtained at comparatively low temperatures, and the presence of an alkali is essential. Excess of cobalt must, of course, be avoided, for the black cobalt oxide completely obscures the green color. A larger proportion of cobalt than is recommended in the procedure may be added without danger, but the test is very satisfactory even when a large excess of zinc is present.

***Procedure 58a.**—To the filtrate from the Na_2O_2 precipitate (P. 52), add HNO_3 (1.20), keeping the solution cool, until it reacts slightly acid and any precipitate just redissolves upon shaking. (See note 1.) Dilute the solution to 100 cc. and transfer it to a strong 200 cc. bottle. Add solid $NaHCO_3$, a little at a time, until the mixture after shaking no

longer turns blue litmus paper red at once; finally add 1.0–1.5 grams solid $NaHCO_3$ (weighed out roughly). Close the bottle with a tightly fitting cork, wire it in, wrap a cloth around the bottle, place it in a vessel of warm water, and boil the water gently for twenty or thirty minutes. Cool the bottle to at least 50° (best by slowly adding cold water to the bath), remove the cork, filter at once, and wash, using suction if the precipitate is large. (Filtrate, *P. 58*b*; precipitate, *P. 58*f*.)

Notes.—(1) If up to this point in the analysis there has been no indication of any of the elements that are to be tested for in the alkaline solution, time may often be saved by determining before treating with $NaHCO_3$ whether any of them are present by proceeding as follows: to one-fourth of the solution, which has been acidified with HNO_3, add NH_4OH (0.96) in small excess, note whether a precipitate forms, and then add a few drops of $(NH_4)_2S$ solution. Even if there is no precipitate, vanadium may be present; to test for this, add 3 cc. NH_4OH (0.90) and completely saturate with H_2S. (See *P. 51*a*.) If the results of these tests show that any of these elements are present, treat the remainder of the HNO_3 solution by the regular procedure. If, on the other hand, the results are negative, no further treatment is necessary.

(2) The alkaline solution is kept cold during the neutralization and an excess of HNO_3 is avoided because chromate in the presence of H_2O_2 and an acid is rapidly reduced to a chromic salt, especially when the solution is hot. This reduction, if complete, would prevent the detection of chromium in the subsequent test. H_2O_2 will, to be sure, not be present, since Na_2O_2 is very rapidly destroyed by the boiling of the alkaline solution in P. 52, except when uranium is also present; in this case the peruranate which is formed by the treatment with Na_2O_2 is not decomposed upon boiling, but breaks up into a uranyl salt and H_2O_2 upon acidification.

(3) The success of this separation depends upon securing the proper concentration of the $NaHCO_3$. Since the $NaHCO_3$ may be at first used up in precipitating zinc, aluminum, and beryllium as well as in neutralizing the free acid, the weighed amount of $NaHCO_3$ is added only after the solution ceases to react distinctly acid. A much larger concentration of $NaHCO_3$ than 1.0 to 1.5 per cent. would not prevent the complete precipitation of zinc or of aluminum, but it would interfere with that of beryllium. Thus with a volume of 100 cc. the precipitation of the beryllium is complete when the concentration of the $NaHCO_3$ is 1 per cent., and 1 mg. can usually be detected when it is 2 per cent., but 3 mg. remain dissolved in a 3 per cent. solution, about 15 mg. in a 5 per cent. solution, and about 150 mg. in a 10 per cent. solution. A smaller concentration of $NaHCO_3$ and a smaller volume than 100 cc. are avoided, in order to prevent as far as possible the precipitation of uranyl vanadate, which may otherwise occur when large quantities of uranium and vanadium (about 100 mg. of each) are simultaneously present. The presence of phosphate or oxalate (or chromate) does not cause the precipitation of uranium, nor otherwise interfere with the analysis. When only small amounts of the elements of this group are present, the separation can be made in a smaller volume, care being taken that the concentration of the $NaHCO_3$ rather than the quantity taken be that prescribed.

(4) If it is desired, the separation may be made in an open flask; but in this case the solution must not be boiled and the $NaHCO_3$ solution should not be stronger than 1 per cent. The process is then best carried out by digesting the mixture on a water bath for 20 to 30 minutes in a flask covered with a watch glass. Under these condi-

tions neither zinc nor beryllium dissolve in significant quantity; but one to two milligrams of aluminum may be completely dissolved. The mixture must not be boiled, for a larger amount of aluminum may then dissolve (as much as five milligrams on one minute's boiling).

(5) When a large amount of aluminum or beryllium is present, two to five milligrams of uranium may be carried down almost completely in the $NaHCO_3$ precipitate, so that in this case uranium has to be tested for in the analysis of the precipitate.

(6) In a dilute solution of $Na^+HCO_3^-$ saturated with CO_2, the hydrogen ion and hydroxyl ion concentrations are both very small and are nearly the same as in pure water. AlO_3H_3, basic $BeCO_3$ and $ZnCO_3$ are completely precipitated because the solubility of these substances is not much increased through removal of the OH^- or $CO_3^=$ by combination with H^+ with formation of H_2O or HCO_3^- (leaving the cathions Al^{+++}, Be^{++} or Zn^{++} in the solution) or through removal of the metal ions by combination with the OH^- with the formation of AlO_2^-, $BeO_2^=$ or $ZnO_2^=$. The higher hydroxides of chromium, and vanadium (chromic and vanadic acids) are soluble polybasic acids, which are so much more highly ionized than H_2CO_3 that they displace it from its salt $NaHCO_3$, forming mainly sodium hydrogen chromate or vanadate. The fact that uranium is not precipitated, even though $Na_2U_2O_7$ is difficultly soluble, may be due to the formation of a complex sodium uranyl carbonate.

***Procedure 58b.**—To the $NaHCO_3$ filtrate add HNO_3 (1.20) until the solution is distinctly acid, avoiding an excess of more than 1 cc. (Colorless solution, absence of *chromium.*) Unless the solution is as colorless as pure water, test one-fourth of it for chromium by adding to the cold solution in a test-tube 2 cc. ether and 0.5–1.0 cc. 3 per cent. H_2O_2 solution. (Blue coloration of the ether layer, presence of *chromium.*) To this mixture add about 5 cc. HNO_3 (1.42). (Red coloration of water layer, presence of *vanadium.*)

If chromium is not present, treat the HNO_3 solution or the part of it not tested with H_2O_2 by *P. 58*c*.

If chromium is present, exactly neutralize the remainder of the HNO_3 solution with NaOH, add 2 cc. HNO_3 (1.20) and then 20 cc. 20 per cent. $Pb(NO_3)_2$ solution; allow the mixture to stand for fifteen to twenty minutes, and filter. (Yellow precipitate, presence of *chromium.*) Saturate the filtrate with H_2S, filter off and reject the precipitate; boil the filtrate for two or three minutes to expel H_2S and to coagulate any sulphur that may separate; filter off and reject the precipitate. In order to oxidize vanadyl salts to vanadate, add bromine water (or if much is required, liquid bromine) until the solution has a permanent reddish color. Boil in a casserole until the bromine is expelled and treat the solution by *P. 58*c*.

Notes.—(1) The $NaHCO_3$ filtrate should not be heated after acidifying because some H_2O_2 may still be present (even though most of it is decomposed in the heating with $NaHCO_3$), which would cause the reduction of chromate, and might thus prevent the detection of even several milligrams of chromium. (See *P. 58*a*, N. 2.)

(2) It is desirable to determine in advance, by making a preliminary test if reces

sary, whether or not chromium is present, for, if it is absent, the addition of the lead salt, and the subsequent removal of the lead with H_2S may be omitted. If lead be added, its removal is necessary before the tests for uranium and vanadium can be made. If the acid solution is perfectly colorless, an amount of chromium exceeding 0.5 milligram may safely be pronounced absent. Uranium and especially vanadium in moderate quantity (20 to 50 mg.) also give yellow solutions. A yellow solution is therefore tested for chromate with H_2O_2. In regard to this test, see P 56, N. 1. The test can be made in only a small portion (one-fourth) of the solution, for it is so delicate that the presence of 0.1 milligram chromium in this portion can be detected. The portion in which the test is made is rejected, because chromium, if present, is reduced to the chromic state by the H_2O_2 in the acid solution, and would therefore not be precipitated by the lead nitrate.

(3) When vanadium is present even in moderately small quantity, the water layer, on the addition of H_2O_2, becomes orange-yellow to orange-red in color, owing to the formation of pervanadic acid. This test for vanadium becomes more delicate when the solution is made strongly acid as is directed; a distinct color is then obtained even when only 0.5 mg. vanadium is present in the portion tested, corresponding to about 2 mg. in the whole solution. (Compare *P. 51*a*, N. 4.) The test is not essential since vanadium is always tested for later; it is introduced here, where it can be made in a moment's time, as an additional confirmation of the presence or absence of that element.

(4) The separation of chromium from vanadium and uranium by $Pb(NO_3)_2$ depends on the relatively small solubility of lead chromate in dilute HNO_3 in the presence of a large quantity of $Pb(NO_3)_2$. Under the conditions described in the procedure, over 100 mg. of vanadium yield no precipitate and only 0.1 to 0.3 mg. of chromium usually remains in solution, though this amount is somewhat increased when a very large quantity of $NaNO_3$ has been introduced. To secure these results, however, care must be taken to use the prescribed quantities of HNO_3 and $Pb(NO_3)_2$, for lead vanadate is also a difficultly soluble substance, and would be quantitatively precipitated in the presence of a much weaker acid, such as acetic acid in the presence of ammonium acetate. Lead uranate would also be precipitated from a neutral or slightly alkaline solution.

(5) The presence of much chloride or sulphate would cause the precipitation of white $PbCl_2$ or $PbSO_4$, which might obscure the yellow color of a small quantity of $PbCrO_4$ and prevent the estimation of the amount of chromium present. These anions will, however, not be present in harmful quantity, if in dissolving the original $(NH_4)_2S$ precipitate (P. 51) the acids are used in the way prescribed, and if in acidifying the solutions in *P. 58*a* and *b*, HNO_3 and not HCl is used, as directed.

(6) The lead which is added to precipitate the chromate must be removed before testing for uranium with Na_2HPO_4 (in *P. 58*c*), since it would give a precipitate of $Pb_3(PO_4)_2$. It is precipitated with H_2S, rather than with $(NH_4)_2SO_4$, because in the latter case enough lead (about 1 mg.) still remains in solution to give a precipitate with Na_2HPO_4.

(7) By the H_2S, vanadic acid is reduced to vanadyl nitrate $VO(NO_3)_2$ slowly in the cold but more rapidly on heating the solution, so that sulphur may be precipitated on boiling the filtrate to expel H_2S. This must be re-oxidized to vanadic acid, for otherwise vanadyl ammonium phosphate would be precipitated with the uranium phosphate in *P. 58*c*. The oxidation by bromine does not take place instantaneously; and a considerable excess of bromine must therefore be used, and the mixture allowed to stand for a few minutes.

***Procedure** 58c.—Make the solution obtained in *P. 58*b* neutral

with NH_4OH, add 5 cc. 30 per cent. acetic acid, 1–2 grams solid $(NH_4)_2SO_4$ (or NH_4NO_3), and then 2 grams solid $Na_2HPO_4.12H_2O$, and heat to boiling. (White precipitate, presence of *uranium.*) Allow the mixture to stand ten to fifteen minutes to coagulate the precipitate, filter, and wash the precipitate with a 5–10 per cent. solution of $(NH_4)_2SO_4$ (or NH_4NO_3). (Precipitate, *P. 58*d*; filtrate, *P. 58*e*.)

Notes.—(1) The precipitation of white uranyl ammonium phosphate, $UO_2NH_4PO_4$, is a delicate test provided the solution be made only moderately acid with acetic acid and a sufficient excess of Na_2HPO_4 be added. The separation from vanadium as vanadic acid is a very satisfactory one; for vanadium, even when present in large quantity (100 mg.), does not precipitate, nor is a small quantity carried down by uranium; on the other hand 0.5 mg. uranium gives a distinct precipitate. The test is a somewhat more delicate one if made in a smaller volume, say 40 cc.; in this case the same quantities of reagents may still be used, and the separation is perfectly satisfactory.

(2) The formation of a precipitate at this point is not sufficient evidence of the presence of uranium, for aluminum, beryllium, and lead will separate as phosphates if they have not been completely removed in previous procedures, and vanadium will precipitate as vanadyl ammonium phosphate if the oxidation by bromine was incomplete. On the other hand a slight turbidity may correspond to an appreciable amount of uranium (0.2 to 0.5 mg.). Therefore the confirmatory test for uranium (*P. 58*d*) should always be tried.

(3) When the solution is made alkaline with NH_4OH a pale yellow precipitate of uranyl ammonium vanadate may separate, and may not dissolve when the acetic acid is added. This, however, has no effect on the separation, since, on boiling, it is converted into the less soluble uranyl ammonium phosphate and vanadic acid.

(4) In the absence of ammonium salts uranium is precipitated as uranyl hydrogen phosphate, UO_2HPO_4, which often separates as a very finely divided precipitate that runs through the filter. The ammonium salt is added to cause the uranium to precipitate as uranyl ammonium phosphate, which coagulates and filters more readily.

***Procedure 58d.**—Dissolve the Na_2HPO_4 precipitate (*P. 58*c*) by pouring a small portion of hot HCl (1.12) repeatedly through the filter, evaporate the solution nearly to dryness, add about 10 cc. nearly saturated NaCl solution, pour into a test-tube, cool, and add 5 cc. 10 per cent. $K_4Fe(CN)_6$ solution. (Dark red precipitate or coloration, presence of *uranium.*)

Notes.—(1) The precipitation of the dark red uranyl ferrocyanide $(UO_2)_2Fe(CN)_6$ is a very characteristic and also a very delicate test for uranium, provided care be taken to avoid any excess of acid. The solution must, however, be distinctly acid, for otherwise the precipitate may not form, owing to the small concentration of the uranyl ion, UO_2^{++}. Uranyl ferrocyanide tends to form a colloidal solution, but the presence of NaCl and HCl soon causes it to coagulate.

Procedure 58e.—Neutralize the filtrate from the Na_2HPO_4 precipitate (*P. 58*c*) with NH_4OH (0.90) and add at least 5 cc. more. Saturate the solution completely with H_2S by passing the gas through it in a small flask for ten or fifteen minutes. (Pink or violet red color, presence of *vanadium.*) Pour the solution through a filter; make it distinctly

acid with acetic acid (or HCl) and heat nearly to boiling. (Dark precipitate, presence of *vanadium.*)

Notes.—(1) In regard to the formation of the sulphovanadate of vanadium in the strongly alkaline solution, the partial precipitation of vanadium sulphide on acidifying, and the action of H_2O_2 on vanadic acid, see the Notes on *P. 51*a*.

***Procedure 58f.**—Heat the $NaHCO_3$ precipitate (*P. 58*a*) with 10–30 cc. HCl (1.06) in a casserole, or dissolve it by pouring the acid two or three times through the filter, boil the solution to expel CO_2, add NH_4OH (0.96) until the solution after shaking smells of it and then 2–3 cc. in excess. Heat the mixture nearly to boiling, filter and wash the precipitate, using suction if it seems desirable. (Precipitate, *P. 58*g*; filtrate, acidify with acetic acid and test for zinc by P. 57.)

Notes.—(1) The zinc remains in the ammoniacal filtrate as a complex ammonia salt, chiefly $Zn(NH_3)_4^{++}Cl_2^{-}$. Aluminum and beryllium are precipitated as hydroxides. The precipitate will also contain any uranyl vanadate that was precipitated in the $NaHCO_3$ separation.

***Procedure 58g.**—Dissolve the NH_4OH precipitate (*P. 58*f*) by pouring a hot 5–15 cc. portion of HCl (1.12) repeatedly through the filter, using another portion of acid, if necessary. Add a volume of ether equal to one and a half times that of the solution. Pass into the mixture in a small flask HCl gas until a single layer results, and until fumes of HCl are copiously evolved, cooling the flask in running water during the progress. Cover the flask and let the mixture stand for fifteen minutes even if no precipitate has separated. (White crystalline precipitate, presence of *aluminum.*) Filter through an asbestos filter (see P. 61) or an ordinary filter supported by a small hardened filter folded with it, after first moistening the filter with a mixture of two volumes of HCl (1.20) and three of ether previously saturated with HCl gas; wash the precipitate once with this mixture. During the filtration and washing keep the funnel covered with a watch glass to prevent evaporation of the ether. (Precipitate, P. 54 to confirm the presence of aluminum; filtrate, *P. 58*h*.)

Notes.—(1) Aluminum chloride, $AlCl_3.6H_2O$, is only slightly soluble in concentrated HCl solutions and the precipitate is complete when ether is added and the mixture saturated with HCl. 0.5 mg. of aluminum can be easily detected in 30 cc. The test is therefore a delicate one. It is also very characteristic; for no other elements of the aluminum group is precipitated by this treatment, except chromium when it is present in moderate quantity.

(2) The ethereal solution of HCl, unlike the concentrated aqueous solution, does not disintegrate filter-paper rapidly, and the filtration can almost always be made with an ordinary filter supported by means of a hardened filter. This filtration is apt to be slow, and it is often advantageous to filter through asbestos with the help of suction.

(3) When the NH_4OH precipitate is small (corresponding to less than 30 mg. Al), it need not be treated by this procedure, but it may be dissolved in a little HCl, and treated directly by *P. 58*h*.

***Procedure 58h.**—Evaporate the filtrate from the HCl precipitate (*P. 58*g*), first on a water-bath under a hood until the ether is expelled, and then over a flame, almost to dryness until nearly all the HCl is expelled; add a little water, make alkaline with NH_4OH, avoiding a large excess, and heat nearly to boiling. (No precipitate, absence of *beryllium.*)

If there is a precipitate, dilute to 30 cc., add enough solid $NaHCO_3$ to make a 10 per cent. solution, heat to boiling, boil for one minute, cool, pass in H_2S for a few seconds, and filter after a few minutes if there is a precipitate. Acidify the filtrate with HCl, boil for two or three minutes to expel CO_2, make the solution alkaline with NH_4OH, and heat nearly to boiling. (White flocculent precipitate, presence of *beryllium*, yellow precipitate, presence of *uranium.*)

Treat this precipitate or a portion of it corresponding to about 20 mg. of beryllium by *P. 58*d*. (Dark red precipitate, presence of *uranium.*) Filter and to the filtrate add NH_4OH. (White precipitate, presence of *beryllium.*)

Notes.—(1) The filtrate from the HCl precipitate may contain besides beryllium, uranium or vanadium (carried down in the treatment with dilute $NaHCO_3$ in *P. 58*a*), aluminum (if care was not taken in precipitating and filtering aluminum chloride), and a little iron (introduced from the reagents). This solution is first tested with NH_4OH to determine if any further treatment is necessary. The treatment with the hot concentrated $NaHCO_3$ solution serves to precipitate the aluminum completely and to dissolve the beryllium and uranium. This method of separation of aluminum and beryllium is a satisfactory one, when, as in the present case, only a small amount of aluminum is present; a large quantity of aluminum, however, retains almost completely a small quantity of beryllium. The $NaHCO_3$ solution must not be boiled for a long time, because, owing to the escape of CO_2 and the formation of free NaOH, the solution becomes alkaline enough to dissolve some aluminum. The reason for the great solubility of beryllium hydroxide in concentrated $NaHCO_3$ solutions is not known. H_2S is passed in to remove the iron, since a small amount of it remains dissolved in the concentrated $NaHCO_3$ solution; the filtrate is sometimes dark green even after repeated filtration, due to the presence of colloidal iron sulphide; to precipitate this, add a small amount of a ferrous salt (say 2 to 4 mg. Fe), shake, allow the mixture to stand several minutes, and then filter, finally passing more H_2S into the filtrate to make sure that the iron has been all removed.

(2) The treatment with $K_4Fe(CN)_6$ described in *P. 58*d* gives a satisfactory separation of beryllium from uranium (and vanadium) provided the amount of beryllium in the solution does not exceed 20 milligrams. When more beryllium is present a gelatinous precipitate separates; on this account it is directed to use only a portion of the NH_4OH precipitate when it is large, but even in this case a small amount of uranium can still be detected, owing to the delicacy of the ferrocyanide test. Vanadium, if present owing to its having been precipitated as uranyl vanadate in the treatment with dilute $NaHCO_3$ (*P. 58*a*), remains with uranium and is precipitated as greenish yellow vanadyl ferrocyanide, but does not obscure the dark red color of the uranium precipitate. It is not necessary to provide for the detection of vanadium at this point, since a large quantity always dissolves in the $NaHCO_3$ treatment.

The Iron Group.

Procedure 61.—Transfer the Na_2O_2 precipitate (P. 52) to a casserole together with the filter if necessary, add 5–30 cc. HCl (1.12), boil gently till the precipitate is dissolved, filter to remove the paper, and evaporate the filtrate to 1 or 2 cc. To decompose the HCl add about 5 cc. HNO_3 (1.42), and boil as long as oxides of nitrogen are given off. Add 5–20 cc. HNO_3 (1.42), heat to boiling, add about 0.5 gram of solid $KClO_3$ and boil gently, adding more $KClO_3$ in small portions if a large precipitate forms. (Dark brown or black precipitate, presence of *manganese.*) Boil gently for a minute or two, and filter through an asbestos filter, made by pouring a suspension of washed asbestos over a compact wad of glass wool in a glass funnel. (See note 4.) Heat the filtrate to boiling, add more $KClO_3$, boil, and filter through the same filter if more of the precipitate separates. Wash two or three times with HNO_3 (1.42) which has previously been freed from the oxides of nitrogen by warming with a little $KClO_3$. Evaporate the filtrate to about 5 cc., but not further, dilute to 20 or 30 cc., and filter the solution if it is turbid. (Precipitate, P. 62; filtrate, P. 63).

Notes.—(1) HCl is used for dissolving the Na_2O_2 precipitate rather than HNO_3. Pure concentrated HNO_3 does not dissolve hydrated MnO_2 except in the presence of filter paper, whereby the HNO_3 is reduced to lower oxides; the action is more rapid with HCl (for the MnO_2 is thereby quickly reduced to manganous chloride with evolution of chlorine.)

(2) By $HClO_3$ in HNO_3 solution (but not by HNO_3 alone) manganous salts are rapidly oxidized to hydrated MnO_2 with formation of chlorine dioxide (ClO_2), which escapes as a yellow gas. The HCl must previously be completely removed by evaporation and boiling with HNO_3, since the oxides of nitrogen resulting from its action on the HNO_3 would continuously dissolve the precipitate.

(3) The separation of manganese in this way from the other metals of this group is entirely satisfactory with the following exceptions. A small quantity of iron (up to 1 mg.) may be completely carried down with a large quantity (500 mg.) of manganese. The same is true in a much higher degree of titanium, of which even 50 mg. may be entirely precipitated with 500 mg. of manganese. Much zirconium is also carried down, but never quite completely. Provision is therefore made (in *P. 62*a*) for the detection of these three elements in the precipitate (if it is large) as well as in the filtrate. If it is not thought necessary to test for zirconium in the precipitate, the certain detection of titanium can be much more quickly accomplished just before precipitating the manganese, by diluting the HNO_3 solution, from which the HCl has been removed, with once or twice its volume of water, and adding 3 cc. of 3 per cent. H_2O_2 solution. An orange-yellow or orange-red color shows the presence of titanium. (See *P. 65*b*, N. 1.) In the absence of HCl iron does not interfere with this test, nor does even a large quantity of nickel or cobalt prevent a distinct change of color from being seen.

(4) In filtering the MnO_2 a cylindrical glass funnel with a small delivery tube is usually employed in quantitative analysis. An ordinary conical funnel is, however, satisfactory, provided the wad of glass wool is made compact and enough asbestos

is used. Filtration will, to be sure, be slow if the glass wool is packed very tightly or if the asbestos mat is very thick, but in that case suction may be applied.

(5) On evaporating the HNO_3 filtrate, titanium and zirconium oxides may separate out, especially if the solution be evaporated almost to dryness. For this reason the solution is evaporated only to about 5 cc., but even then a small white precipitate will sometimes be obtained when these elements are present in large amount.

Procedure 62.—Transfer the whole of the $HClO_3$ precipitate (P. 61) if it is small (containing less than 5 mg. Mn), or 5–10 mg. of it if it is large, to a casserole; add 1 or 2 grams solid PbO_2, and about 10 cc. HNO_3 (1.20); boil for about two minutes in a casserole covered with a watch glass; pour the mixture into a test-tube, and allow the PbO_2 to settle. (Violet red solution, presence of *manganese.*)

If the precipitate is large, dissolve the remainder in hot HCl (1.12) in a casserole, or by pouring a 10–15 cc. portion repeatedly through the filter, and boil the solution to expel chlorine. To one-tenth of this solution add 5 cc. KCNS solution. (Deep red color, presence of *iron.*) Treat the remainder of the HCl solution by *P. 62*a* to recover any titanium and zirconium that may be present.

Notes.—(1) This confirmatory test for manganese is usually superfluous since the precipitation of MnO_2 by $HClO_3$ is highly characteristic. In order that the PbO_2 test may be satisfactory, the HNO_3 used must be fairly concentrated and the boiling continued for two or three minutes.

***Procedure 62a.**—To the HCl solution (P. 62), without evaporating it, add NH_4OH (0.96) until the mixture is barely alkaline, avoiding the addition of more than two or three drops in excess; heat nearly to boiling for two or three minutes, filter at once, and wash with hot water. Reject the filtrate. Dissolve the precipitate in a little hot HCl (1.12) (without diluting it with water), reserve it, and unite it with the main HCl solution to be treated in *P. 65*a*.

Notes.—(1) In order to avoid as far as possible the precipitation of manganese by NH_4OH, the OH^- concentration is kept small by avoiding an excess of NH_4OH and by having a large quantity of ammonium salt present. Under these conditions the oxidation by the air to the manganic state is slow. If, however, much NH_4OH be added, oxidation takes place rapidly and much manganese may be precipitated as $Mn(OH)_2$, yielding a brown precipitate. Even at best a little manganese will come down, but a moderate amount does not interfere with the subsequent tests for titanium and zirconium.

Procedure 63.—Add about one-tenth of the HNO_3 solution (P. 61) to three or four times its volume of ammonium molybdate reagent, and heat to 60–70°. (Yellow, finely crystalline precipitate, presence of *phosphate.*) If there is no precipitate, or only a very small one, treat the remainder of the HNO_3 solution by P. 64; otherwise by P. 65.

Notes.—(1) Phosphate is tested for at this point because a different treatment is necessary when it is present in significant amount, in order to separate from it alkaline-earth elements and to provide for their detection. When phosphate is not pres-

, iron, thallium, titanium, and zirconium can be separated from nickel, c
l the alkaline-earth elements by NH_4OH (as in P 64); but, when conside
osphate is present, the alkaline-earth elements would be partly or wholly p
ed in combination with it. (See P. 51, N. 6.)
2) In order that the phosphate test may be delicate and may appear immedi
arge proportion of the molybdate reagent must be used and the solution m
rmed. The precipitate of ammonium phosphomolybdate is of complicate
newhat variable composition; it contains ammonium phosphate and mo
d, approximately in the proportion $(NH_4)_3PO_4:12MoO_3$.

Procedure 64.—If phosphate is absent, make the HNO_3 sol
. 62) strongly alkaline with NH_4OH (0.96) using an excess of 3-
ark red precipitate, presence of *iron*.) Filter, and wash the
ipitate, using suction if the precipitate is large, and sucking it a
possible.
Treat the filtrate by P. 66.
Dissolve the precipitate in HCl (1.12), warming if necessary, t
re not to dilute the acid by wash water. To about one-tenth c
ution add 5 cc. KCNS solution. (Dark red color, presence of
Treat the remainder of the solution by *P. 65*a*.

Notes.—(1) If titanium and zirconium are to be tested for, it is important
ve the NH_4OH precipitate in HCl of a specific gravity 1.12 (24 per cent. HC
avoid dilution, for the separation in *P. 65*a* depends on the concentration of th
2) The red color obtained on adding KCNS is due to the formation of un-i
ic thiocyanate, $Fe(CNS)_3$. This test may be made in the presence of
l, for the acid HCNS is also a highly dissociated acid, which is therefore n
ced from its salt. Much HNO_3 must not, however, be present; for, by its
KCNS, NO_2 may be formed and this also gives a deep red color with KCNS.
t for iron is an extremely delicate one; and if only a faint color is obtained, th
d in the process must be tested for iron.

Procedure 65.—When phosphate is present, test one-tenth o
NO_3 solution (P. 63) for iron, by evaporating it just to dryness, a
2 cc. HCl (1.20), evaporating again to decompose the HNO_3, dil
5 or 10 cc. and adding 5 cc. KCNS solution. (Permanent red
esence of *iron*.) To the remainder of the solution add NH_4OH
til the precipitate formed by the last drop does not redissol
aking. If, owing to the addition of too much NH_4OH the sol
comes alkaline or a large precipitate separates, make it disti
id with acetic acid. Add 5 cc. of a 50 per cent. solution of ammo
etate, and, unless the mixture is already of a brownish red colo
per cent. $FeCl_3$ solution drop by drop until such a color is prod
ld enough water to make the volume about 100 cc., boil in a 2
sk for five minutes, adding more water if a very large preci
parates, and let the mixture stand for a minute or two. Filter
ll hot, and wash with hot water. Add 3–5 cc. more ammo
etate solution to the filtrate, boil it again, and collect on a sep

filter any further precipitate. Make the filtrate alkaline with NH_4OH, adding an excess of 2–3 cc., filter off and wash any precipitate, uniting it with the main precipitate. (Filtrate, P. 66; precipitate, reject or dissolve in hot HCl (1.12), and treat by *P. 65*a*.)

Notes.—(1) With regard to the test for iron with KCNS and the necessity of removing the HNO_3, see P. 64, N. 2.

(2) This method of separation depends on the facts that, upon boiling an acetic acid solution containing much acetate, ferric iron and titanium are completely precipitated, and thallic thallium and zirconium nearly so, in the form of a basic acetate or hydroxide; and that all the phosphate present combines with these elements when they are present in excess, and therefore it then passes completely into the precipitate, leaving the bivalent elements in solution. This behavior of the phosphate is due to the fact that the solubility in acids of the phosphates of the trivalent and quadrivalent elements is much smaller than that of the phosphates of the bivalent elements.

(3) If upon adding the ammonium acetate the solution becomes of a reddish color, it shows that iron is present in quantity more than sufficient to combine with the phosphate; for a cold solution containing ferric acetate is of a deep red color. If, on the other hand, a colorless solution results (either with or without a precipitate), it shows that there is no excess of iron, and $FeCl_3$ is therefore added, which causes the precipitation of $FePO_4$ as a yellowish white precipitate. Upon boiling, the excess of iron separates completely as a dark red gelatinous precipitate of basic ferric acetate, leaving the supernatant liquid colorless, except when nickel or cobalt is present.

(4) The solution is diluted to at least 100 cc., owing to the large volume of the precipitate, and it must be heated in a capacious flask owing to its tendency to boil over.

(*5) Zirconium may not be completely precipitated under the conditions of this procedure, 1–5 mg. sometimes remaining in solution, especially when considerable acetic acid is present. To ensure its complete separation, the filtrate is made alkaline with NH_4OH.

(*6) The precipitation of thallium in this procedure is not quite complete, but there is no danger of losing even 0.5 of a milligram when iron is also present, as is always the case.

***Procedure 65a.**—To the HCl solution (P. 64 or 65, and *62*a*) which should be of specific gravity of 1.11–1.12, add 10–20 cc. more HCl (1.12), transfer the (cold) solution to a separating funnel, add an equal volume of ether, shake vigorously several times (preferably after inverting the funnel and opening the cock), and then allow the two layers to separate. Draw off the layers separately, and rinse out the funnel with a little ether. Return the aqueous layer to the funnel and treat it with ether as before; if necessary, repeat this treatment once or twice until the ether layer remains colorless. (Water solution, *P. 65*b*; first ether solution, *P. 65*d*; remaining ether solutions, reject.)

Notes.—(1) If the directions are followed, 97 to 99 per cent. of the $FeCl_3$ present passes into the ether layer in each extraction. It is evident from this statement, that even when 500 mg. of iron are present, substantially all of it will be removed in three extractions. But it is important that the concentration of the HCl solution in contact with the ether layer lie within the narrow limits of 20 to 22 per cent. HCl, corresponding to a specific gravity of 1.10 to 1.11 at 15°. This concentration is realized

in the procedure, even though a little stronger acid is used, for some of the HCl passes into the ether layer. The extraction of the $FeCl_3$ is less complete both with stronger and weaker HCl solutions; thus with HCl containing initially either 18 or 25 per cent. about 94 per cent. of the $FeCl_3$ passes into the ether layer; while with 8 per cent. HCl only 4 or 5 per cent. of the $FeCl_3$ was extracted in each shaking. Almost all the thallium, which is present as $TlCl_3$, also passes into the first ether extract.

(2) The following are probably the principles involved in this ether extraction. Since iron passes into the ether layer only in the form of $FeCl_3$, the quantity of it extracted by the ether increases, in accordance with the distribution law, the larger the proportion of un-ionized anhydrous $FeCl_3$ in the water layer. This proportion is, however, increased by increasing the concentration of HCl both in virtue of the reduction of the ionization by the common-ion effect and of the reduction of the hydrolysis of the ferric salt by the free acid. It is doubtless true that the strong acid has also a dehydrating effect, thereby increasing the anhydrous $FeCl_3$ in the water layer. As the HCl becomes very concentrated, however, another effect, opposite in character, comes into play; namely ether dissolves in large quantities in the aqueous layer, and HCl and water dissolve in large quantity in the ether layer, thus making the two layers more nearly alike, and doubtless decreasing the distribution-ratio for the $FeCl_3$ between the ether and water layers. With respect to this explanation, it should be added that it is uncertain to what extent complex acids ($HFeCl_4$, etc.) may be involved.

(3) Since the color of the ether layer is a sensitive indication of iron, the treatment with ether may be discontinued as soon as a nearly colorless ether extract is obtained. When titanium is present the water layer may remain distinctly yellow, owing to the presence of hydrogen peroxide as impurity in the ether; such a color does not, therefore, show that iron is still present.

(4) Titanium and zirconium remain completely in the water layer. When much zirconium is present some of it may be precipitated out, as chloride; but this remains suspended in the water layer.

(5) Phosphoric acid does not interfere with this separation, and the iron can therefore be extracted even after the basic acetate procedure.

***Procedure 65b.**—Heat the HCl solution (*P. 65*a*) on a waterbath until the ether is expelled, add 1 cc. H_2SO_4 (1.20), evaporate almost to dryness until the H_2SO_4 begins to fume, adding 1 cc. more H_2SO_4 (1.20) if the residue is solid. If the residue is dark colored, owing to organic matter, add a few drops HNO_3 (1.42) and evaporate again until the H_2SO_4 begins to fume. Cool, add 5 cc. water, 10 cc. 3 per cent. H_2O_2 solution, and then 10 cc. 10 per cent. $Na_2HPO_4.12H_2O$ solution. (Orange-yellow to orange-red solution, presence of *titanium;* white, flocculent precipitate, presence of *zirconium.*) Let the mixture stand for at least an hour, filter, and wash the precipitate. (Filtrate, if colored, *P. 65*c*; precipitate, note 3.)

Notes.—(1) By the addition of H_2O_2 titanium is converted into a sulphate corresponding to the higher oxide TiO_3, the red color being due to the cathion. This color test is an extremely delicate one, even 0.1 mg. Ti imparting a distinct, yellow color to the solution.

(2) By the Na_2HPO_4, zirconium is precipitated as a basic phosphate, $Zr(OH)PO_4$. Its precipitation is slow; but, if nothing has separated after half an hour, it is safe to conclude that less than 0.5 zirconium is present, provided care has been taken not to use more H_2SO_4 than is directed in the procedure. If the titanium had not been

oxidized by the addition of H_2O_2, it would also give an entirely similar precipitate of $Ti(OH)PO_4$; but from a solution containing H_2O_2 in excess when titanium is alone present none of it separates even on standing several hours. When zirconium and titanium are present together, a small proportion of the titanium is carried down with the zirconium and the phosphate precipitate may then have a distinct, yellow color.

(3) Some of the rare earth elements, such as thorium, may also be precipitated as phosphate at this point, if these elements have not been proved absent or removed in *P. 52*a*. In such a case the presence of zirconium may be proved by pouring a portion of dilute HF several times through the filter (supported in a celluloid funnel or a platinum ring), evaporating with H_2SO_4 in a platinum dish, diluting, and adding NH_4OH. The rare-earth phosphate would be left undissolved by the HF.

(4) Besides titanium and zirconium, the solution from *P. 65*a* will sometimes contain uranium, manganese, and cobalt (carried down in the precipitates in P. 52, *P. 62 *a*, and P. 64, respectively); but not in sufficient amount to interfere with the zirconium and titanium tests. The only other element of the aluminum and iron groups that gives a similar color with H_2O_2 in acid solution is vanadium; but this, aside from the fact that it should not be present, would give no precipitate with Na_2HPO_4 (not even on the addition of Na_2SO_3 in *P. 65*c*).

Procedure 65c.—To the H_2O_2 solution (*P. 65*b*), if colored, add powdered Na_2SO_3 little by little until the solution is decolorized, and let the mixture stand twenty or thirty minutes. (White flocculent precipitate, presence of *titanium.*)

Notes.—(1) This test serves to confirm the presence of titanium and to enable the quantity of it to be better estimated. H_2O_2 and the sexivalent titanium compound are rapidly reduced by the action of H_2SO_3, even in the cold, and titanium then precipitates as $Ti(OH)PO_4$. As in the case of zirconium, the precipitation takes place slowly. When there was only a faint color with H_2O_2, no precipitate will be obtained; but 0.5 mg. of titanium is easily detected, if the concentration of the sulphuric acid does not exceed 1 cc. H_2SO_4 (1.20) in 25 cc. solution.

***Procedure 65d.**—Evaporate the first ether extract (*P. 65*a*) on a waterbath, and dissolve the residue in 3–5 cc. H_2SO_4 (1.20) and 3–5 cc. water. To the cold solution in a test-tube add 2–3 cc. 1 per cent. KI solution and powdered Na_2SO_3 a little at a time until the iodine color has permanently disappeared. (Yellow precipitate, presence of *thallium.*) Filter, using preferably a hardened filter when the precipitate is small. Collect a little of the precipitate on a clean platinum wire and introduce the wire into a colorless gas flame. (Momentary green flame, presence of *thallium.*)

Notes.—(1) The precipitation of thallium as TlI is practically complete, provided that the volume of the solution is small, say less than 15 cc. The presence of iron does not prevent a good blank being obtained, nor does its presence in large quantity (500 mg.) prevent the detection of 0.5 mg. of thallium. TlI is readily oxidized to the soluble TlI_3 by iodine; therefore an excess of sulphite must be present.

(2) Any quantity of thallium in excess of 10–15 mg. is precipitated in P. 11, except when the solution there treated with HCl contains the thallium in the thallic state.

(3) The green flame test is a very delicate and characteristic test, but, on account

of the volatility of the thallium compound, the green color is seen only at the moment in which the wire is introduced into the flame. A hardened filter is recommended when the precipitate is small, because the precipitate can be more readily collected on the wire on account of the smooth surface of the filter.

Procedure 66.—Into the ammoniacal solution (P. 64 or P. 65) pass H_2S gas until the mixture after shaking blackens lead acetate paper held above it. (Black precipitate, presence of *nickel* or *cobalt*.) Filter, and wash the precipitate with water containing a very little $(NH_4)_2S$. (Precipitate, P. 67; filtrate, P. 81.)

Notes.—(1) In precipitating NiS, the use of H_2S has the advantage that the nickel is all thrown down at once, while with $(NH_4)_2S$ some of it usually remains in the solution, giving it a dark brown color. If found more convenient, $(NH_4)_2S$ can of course be used, the filtrate being boiled to throw down the unprecipitated nickel, as described in P. 51.

(2) The filtrate is in general tested for the alkaline earth elements, for these may be precipitated with the aluminum and iron groups when phosphate or certain other acid radicals are present, as discussed in P. 51 N. 6 and 7.

Procedure 67.—Transfer the H_2S precipitate (P. 66) with the filter to a casserole, and add 10–30 cc. of a cold mixture of 1 volume HCl (1.12) and 5 volumes of water. Digest in the cold for five minutes, stirring the mixture frequently, and filter.

Treat the residue by P. 68.

Boil the HCl solution until the H_2S is completely expelled, add 10 per cent. NaOH solution until the mixture is slightly alkaline, transfer to a casserole, cool, and add 0.5–1 gram Na_2O_2 a small portion at a time. Boil for several minutes to decompose the excess of Na_2O_2 and cool the mixture; filter off the precipitate, and treat it by P. 68, uniting with it the residue already obtained in the HCl treatment. Make the solution acid with acetic acid, warm it to about 60°, and pass in H_2S for two or three minutes. (White flocculent precipitate, presence of *zinc*.) Apply to the precipitate the confirmatory test as described in P. 57.

Notes.—(1) This treatment with dilute HCl serves to extract almost completely the zinc which may be present in this precipitate, owing to its having been carried down in the Na_2O_2 precipitate as described in P. 52, N. 11. A small proportion of the nickel and cobalt present (5 to 20 per cent.) always dissolves in the dilute HCl, and the subsequent treatment with Na_2O_2 serves to separate them from the zinc. This separation is satisfactory when, as in this case, the nickel and cobalt are present in such small quantity that only an insignificant quantity of zinc is carried down with them. When, therefore, the H_2S precipitate is small, it may, instead of being treated with dilute HCl, be dissolved at once in *aqua regia* and the solution treated directly as described in the last paragraph of the procedure.

(2) This procedure must always be followed in order to determine whether or not zinc is present in the substance, except in the case that a satisfactory test for it has already been obtained in P. 57, or in the case that the original Na_2O_2 precipitate (P. 52) was small.

Procedure 68.—Transfer the residue insoluble in dilute HCl, and the

Na_2O_2 precipitate (P. 67), with the filters to a casserole, add 5–15 cc. HCl (1.12) and a few drops HNO_3 (1.42), warm until the black precipitate is dissolved, and filter off the paper. Evaporate the solution nearly to dryness to expel most of the acid, add about 5 cc. water, and then NaOH solution drop by drop until the mixture is neutral, or until a permanent precipitate just forms. Test one-half of this mixture for cobalt by P. 69, and the remainder for nickel by P. 70.

Procedure 69.—To one-half of the neutral solution (P. 68) add 15 cc. 30 per cent. acetic acid, and then 50 cc. 30 per cent. KNO_2 solution; dilute to 100 cc., and allow the mixture to stand at least half an hour if no precipitate forms sooner. (Yellow, finely divided precipitate, presence of *cobalt.*) Filter, and wash with KNO_2 solution. If the precipitate is very small, incinerate the filter. Introduce a portion of the precipitate, or of the ash, into a borax bead made in the loop of a platinum wire, and heat strongly, adding more of the precipitate or ash if no color is obtained. (Deep blue color, presence of *cobalt.*)

Notes.—(1) The yellow precipitate is potassium cobalti-nitrite, $K_3Co(NO_2)_6$, which in solution dissociates into K^+ and the complex anion $Co(NO_2)_6^{=}$. The precipitate is somewhat soluble in water but very difficultly soluble in a concentrated KNO_2 solution, owing to the common ion effect of the potassium ion. In the formation of this substance the cobaltous salt is oxidized to the cobaltic state by the nitrous acid displaced from its salt by the acetic ion, the cobaltic salt combining as fast as formed with the potassium nitrite, according to the equations:

$$Co^{++}(NO_2^-)_2 + 2HNO_2 = Co^{+++}(NO_2^-)_3 + H_2O + NO \text{ and}$$
$$Co^{+++}(NO_2^-)_3 + 3K^+NO_2^- = K_3Co(NO_2)_6.$$

(2) The formation of the $K_3Co(NO_2)_6$ precipitate takes place slowly, but even when very little cobalt is present (0.1 to 0.2 mg.) a distinct test is obtained within ten minutes; but the complete precipitation of a large amount of cobalt requires several hours, so that the method is ill-adapted for the removal of cobalt before testing for nickel. Moreover, when nickel is present, some of it is carried down with the cobalt, and this is true even when the total amount of nickel is small. For these reasons the test for nickel is made in a separate portion.

(3) Nickelous salts are not oxidized by nitrous acid, and are not precipitated by KNO_2 except in a very concentrated solution, when a dark yellow to dark red precipitate of potassium nickelous nitrite, $K_4Ni(NO_2)_6$, may separate. By making the volume large, as directed in the procedure, there is no danger of the precipitation of nickel.

Procedure 70.—To the remainder of the neutral solution (P. 68) add 10 per cent. KCN solution, a few drops at a time, until all or nearly all of any precipitate that may form at first redissolves; then add 0.5–3 cc. more (according to the amount of the KCN precipitate). Heat to 50° or 60° in an open casserole, with frequent stirring, for five minutes, or longer if the solution has not become light-colored. Filter off and reject any small precipitate that may remain. To the filtrate, preferably in a test-tube, add freshly prepared, concentrated NaBrO

solution (see note 3) until a piece of filter paper moistened with and starch solutions, when dipped into the solution, is colored blu brown. Allow the mixture to stand five to ten minutes, and fi (Brown to black precipitate, presence of *nickel.*)

Wash the precipitate; dissolve a small portion of it, if it is larg 2–3 cc. HNO_3 (1.20); add 3–5 cc. 10 per cent. tartaric acid solut neutralize with 10 per cent. NaOH solution, and add 3 or 4 cc. in cess. Pass in H_2S for about one minute, filter out any precipitate may form and saturate the filtrate with H_2S. Filter again if there precipitate. (Brown coloration, presence of *nickel.*)

Notes. -(1) The reactions involved in the first test for nickel are as follows: a little KCN is added to the neutral solution, precipitates of (green) $Ni(CN)_2$ and brown) $Co(CN)_2$ result except when only small amounts of these elements are pr The addition of more KCN causes the precipitate to dissolve owing to the form of soluble complex cyanides, as $K_2^+[Ni(CN)_4]^=$ and $K_4^+[Co(CN)_6]^{====}$. The plex nickel salt is stable in the air, but the cobalt salt is very readily oxidized a ing to the equation:

$$2K_4^+[Co(CN)_6]^{====} + O + H_2O = 2K_3^+[Co(CN)_6]^{\equiv} + 2K^+OH^-.$$

(Potassium cobaltocyanide) (Potassium cobalticyanide)

The first action of the NaBrO is to decompose the excess of KCN, chiefly with form of KCNO. It then oxidizes the nickel to the nickelic state, whereupon the nickel mediately precipitated as brownish-black $Ni(OH)_3$ by the NaOH present. Th balt, though already in the cobaltic state, is not precipitated as $Co(OH)_3$, be the complex ion, $[Co(CN)_6]^{\equiv}$, is so slightly ionized into its constituent-ions (Co and 6 CN^{---}) that the concentration of the Co^{+++} does not suffice to produce the OH^- present the solubility-product for the $Co(OH)_3$, and that of the CN^- small that it is only very slowly oxidized by the NaBrO.

(2) In executing this procedure the following precautions should be observe very large excess of the strong KCN solution over that required to redissolve th cipitate should not be added, for the excess must be destroyed by the NaBrO the nickel can be oxidized and precipitated by it. Yet there must be sufficient added, not only to combine with all the cobalt, but to furnish a moderate exc order that the oxidation to the cobalticyanide may take place rapidly. Care also be taken to heat the solution long enough in the air to complete this oxid before the NaBrO is added, for otherwise the latter reagent after destroying th KCN will oxidize the decomposable cobaltocyanide with precipitation of Co(just as it does the nickelocyanide; the completion of the oxidation by the air dicated by the disappearance of the dark color in the solution. Finally one make sure (by applying the iodide-starch test) that an excess of NaBrO ove required to oxidize both the cyanide and the nickel has been added. If thes cautions are observed, there is no difficulty in securing a precipitate with 0.2 m nickel nor in causing 300 mg. of cobalt to remain entirely in solution.

(3) The hypobromite reagent is prepared by adding liquid bromine to a k volume of 10 per cent. NaOH solution until the solution becomes distinctly red, to the presence of excess of bromine; and then adding half as much more NaOH tion. This solution may be filtered through a hardened filter. It decomposes rapidly, with formation of bromate and bromide, and also with evolution of ox and should therefore not be used when more than a few days old. Instead o

reagent, bromine water and NaOH solution may of course be used. The concentrated hypobromite solution is recommended because a much smaller volume of it is required to decompose the large excess of cyanide used in the procedure.

(4) When an alkaline tartrate solution containing a small amount of nickel (even 0.1 to 0.2 mg. in 20 cc.) is saturated with H_2S a clear brown solution is obtained. With somewhat larger amounts of nickel (10 to 20 mg.) the liquid is opaque but runs through a filter very readily. The condition of the nickel in this solution is not known. The presence of the tartrate serves merely to prevent the precipitation of $Ni(OH)_2$ by the NaOH solution, owing to the formation of a complex salt containing the nickel in the anion. The brown color does not appear until the alkaline solution is nearly saturated with H_2S, so that care must be taken to use an excess of H_2S.

(5) This confirmatory test for nickel is not interfered with by moderate amounts of other elements of this group, such as cobalt and iron (which, however, should not be present at this point), for on leading H_2S into an alkaline tartrate solution containing these elements, they are completely precipitated as sulphides and may be filtered off, yielding a filtrate which in the absence of nickel remains clear when saturated with H_2S, or becomes dark brown when it is present in even small amounts.

Test Analyses.

Numerous analyses were made to test the efficiency of the process above described. Nearly all of those which were made after the procedure assumed final form are reproduced in the tables below. Almost all the analyses relating to the common elements alone were made before the procedures for the rare elements had been worked out, but the process for the analysis of mixtures containing only the common elements was at that time substantially the same as given above. In these tables the numbers in each vertical column show the weights in milligrams of the various elements which the solution submitted to analysis contained. The results of the tests for each element are shown by the letters following these numbers. That the result was satisfactory is indicated by the letter S; that is, when the element was present, that the test for it, however small, was unmistakable, and therefore conclusive; and when the element was absent, that a good blank test was obtained. When the test was very small, especially in comparison to the quantity of the element present, though still unmistakable, this is sometimes indicated by the symbol S–. When in the presence of the element the test failed, or in its absence a result was obtained that might be thought to indicate its presence, the letter F is used. When the result was doubtful or inconclusive, owing to the appearance or small size of the precipitate, this is indicated by the letter D. When the test was not tried, if the element was present a dash is used in place of a letter; or, if the element was not present, dots are inserted.

Common Elements.

The following analyses (Nos. 114–119) were begun at P. 51; P. 61 was introduced before P. 52.

.. No.	114.	115.	116.	117.	118.	119
n.....	10 S	2 S	1 S	500 S	500 S	0 S
....	10 S	2 S	1 D^1	0 D^1	2 S	0 I
....	10 S	2 S	1 S	0 S	2 F^2	0 S
1...	10 S	2 S	1 S	0 S	2 S	0 S
:	10 S	2 S	1 S	0 S	2 S	500 S
i.....	10 S	2 S	1 S	0 S	2 S	0 S
)....	10 S	2 S	1 S	0 S	..	0 S

alyses 120–125 were begun at P. 61.

No.	120.	121.	122.	123.	124	1
... .	500 S	500 S	100 S	1 S	....	
. .. . . .	0 S	1 S–	1 S	100 S	500 S	500
.....	2 S	1 S	....	....	3 S	1

alyses 125–127 were made by P. 69; analyses 128–130 by P.

.. No.	126.	127	128.	129.	130.
).... ..	0 S	0 5 S	150–	150–	150–
i..... ..	250–	250–	0 S	0.3 S	0.15 S

: following analyses (Nos. 131–143) were begun at P. 52.

.. No.	131.	132.	133.	134.	135.
.....	0 S^2	0 S^2	0 S^2	0 S^2	0 S^2
.....	2 S	1 S	0 S	....	0 S
1 P. 57.	2 F	4 F	10 F	20 S–[5]	5 F
1 P. 67.	S	S	S	S	S
.....	500 S	500 S	500 S	500 S	0 S
. . ....	0 S	0 S	0 S	0 S	500 S
.... .	0 S	0 S	0 S	0 S	0 S

.. No.	137.	138.	139.	140.	141.	142.
.... . .	.. .	..	....	....	....	200 S
. P. 57...	5 F	5 S–[7]	10 S–[6]	3 F	5 S–[5]	5 F^6
) P. 67. .	S	S	–	–	–	–
.....	500 S	500 S	500 S	. ..	....	....
....	....	....	. ..	250–	250–	250–
. .....	....	....	...	250–	250–	250–

: following analyses (Nos. 144–155) were begun at P. 52; P. 6
ed.

.. No.	144.	145.	146.	147.	148.
... .	0 S^2	3 S	3 S	0 S^2	0 S^2
... ...	0 S	2 S	1 S	1 S	0 S
P. 57.... .	0 S	5 S–[5]	3 F	3 S–	3 F
. P. 67.....		S	S	S	S
.....	0 S	200 S	200 S	100 S	100 S
.....	500 S	500 S	500 S	100 S	100 S
....	0 S	2 S	1 S	0 S	....
.. ..	0 S	2 S	1 S	0 S	100 S
....	0 S	2 S	1 S–	0 S	0 S
....	0 F^6	0 F^6	0 F^6	4 S	0 F^6
.. . .	0 S	2 S	1 S	2 S	2 S

T. A. No.	150.	151.	152.	153.	154.	155.
Cr	2 S	....	0 S	....	2 S	1 S[10]
Zn in P. 57	3 F	5 S	0 S	1 F	....	....
Zn in P. 67	3 –	5 S	0 S	1 S	....	....
PO_4	100 S	100 S	....	....	....	....
Fe	100 S	100 S	0 S	....	....	....
Co	100 S	100 S	500 S	500 S	....	....
Ba	2 S	1 F	....	....	100 S	100 S

Mixtures Containing the Rarer Elements.

Analyses 156–161 were begun at *P. 58*a*.

T. A. No.	156.	157.	158.	159.	160.	161.
Cr	0 S	0 S	2 S	1 S[11]	....	....
U	100 S	0 S	100 S	100 S	100 S	1 S
V	0 S	100 S	100 –	100 –	1 S	100 S

Analyses 162–165 were begun at *P. 58*f*.

T. A. No.	162.	163.	164.	165.
Al	500 S	500 S	1 S	1 S
Be	0 S	2 S[12]	0 S	100 S

Analyses 166–170 were begun at *P. 58*a*.

T. A. No.	166.	167.	168.	168*a*.	169.	170.
Zn	....	....	....	....	200–	200 S
Al	200–	200–	....	....	....	200 S
Be	....	....	50–	50 S	....	....
U in *P. 58*c–d*.	2 F	3 S–	2 F	2 S–	2 S	2 F
U in *P. 58*h*	2 –	3 –	2 –	2 S–	2 S–	2 S

Analyses 171–176 were begun at P. 64; analysis 176 at P. 52.

T. A. No.	171.	172.	173.	174.	175.	176.
Al	....	....	....	....	....	200–
Mn	....	....	....	....	....	200 S
Fe	500 S	500 S	0.5 S	500 S	500 S	200 S
Ti	0 S	1 S	5 S	....	....	....
Zr	0 S	1 S	....	....	....	....
Tl	0 S	....	....	1 S	0.5 S	1 S[13]

The following analyses (Nos. 177–181) were made by Mr. R. D. Gale, who had had no previous experience in connection with the process. The first analysis was with a known mixture, the remaining four were with unknowns. Mr. Gale received no assistance while making an analysis (except in T. A., No. 179), but all the precipitates and solutions were preserved in order that the causes of mistakes might afterwards be investigated. The process was practically in its final form with exception of the procedures relating to the separation of chromium, uranium and vanadium (*P. 58*b–e*), which were revised on account of the results of these analyses; moreover, uranium was not tested for in *P. 58*h*. Test analyses 156–161 and 166–170 were made at a later date to test these procedures in their final form.

T. A. No. Begun at—	177. P. 52.	178. P. 51.	179. P. 51.	180. P. 52.	181. P. 5
.. ..	2 S	1 S–[16]	1 S	1 S	2
....	3 S	1 F[16]	1 F[16]	0 S	100
. ...	3 S	1 S	1 S	0 S	100
in P. 57...	3 S	1 F	1 S	1 F	100
in P. 67....	3 D	1 S–	1 ..	1 S–	100
....	3 S	200 S	1 S[17]	0 S	0
. ...	3 S	1 S	0.5 S	0 S	0
. ...	3 S	1 S	1 S	200 S	300
4	....	....	....	320 S	.
... .	3 S	200 S	1 S	1 S[18]	1
....	3 S	1 S	0 5 S	1 S	0
....	3 S	1 S–	1 S	1 F[22]	0
....	3 S–[20]	1 S	1 S	200 S	1
... ...	3 S–[20]	200 S	1 S	1 S	1
.. ..	. .	.. .	....	200 S	..
. . . .	. ..	....	....	2 S	....

Notes.—(1) The presence of aluminum in the reagents made the result doubtful.
2) A distinct precipitate of $Al(OH)_3$ was obtained in P. 53, but not more than with the re
ne.
3) Excess of HCl was added in P. 53 and the solution boiled, as a result of which the ch
l was reduced. On analyzing another mixture, and using HNO_3, a satisfactory test for chro
obtained.
4) The absence of manganese was confirmed by fusing some of the iron salt on platinum foi
CO_2 and KNO_3: no green color was obtained.
5) A small precipitate of ZnS was obtained in P. 57, which did not contain more than 1 m
C. E., P. 52, N. 11.
6) A small precipitate of ZnS was obtained in P. 57, corresponding to 2 or 3 mg. Zn.
7) In this analysis a large excess of alkali was added before the Na_2O_2 in P. 52, and the
well stirred.
8) This analysis was repeated except that the acid solution in P. 42 was poured slowly i
ess of hot alkali before adding Na_2O_2: a distinct test for zinc was then obtained in P. 57.
9) A distinct test for calcium was obtained (except possibly in T. A. No. 148): the iron s
nd to contain about 2 mg. Ca with 500 mg. Fe.
10) This analysis was repeated except that no Na_2CO_3 was added in P. 52: the test for chro
ed.
11) See C. E., *P. 58*b*, N. 2.
12) The precipitate of $Be(OH)_2$ obtained in *P. 58*h* was large and corresponded to 2 mg. Be
wing that much smaller amounts could be easily detected.
13) The basic acetate procedure (P 65) was used instead of P. 64 good tests for thallium
ained both in the precipitate and in the filtrate (Compare C. E., P. 65, N. 6.)
14) Chromium was lost in *P. 58*a*, owing to the presence of H_2O_2 (from the perurauate,
P. 52, N. 6 and *P. 58*b*, N. 2) and the addition of a large excess of acid.
15) A slight blue coloration was obtained with H_2O_2 in *P. 58*b*, corresponding to not mor
mg. Cr. No lead nitrate was added.
16) The directions in *P. 58*c* were faulty too little phosphate was added to precipitate 1
17) A good test for aluminum was obtained in *P. 58*g*, but the confirmatory test (P. 54)
18) The test for iron in P. 65 was a failure: the iron was found with the manganese in P
19) Satisfactory tests for iron were obtained in P. 62 and in P. 64.
20) $(NH_4)_2S$ was used instead of H_2S in precipitating the sulphides in P. 66, and some nic
in the brown solution. Nickel and cobalt were also lost in P. 67 in the treatment with
l, owing to the rejection of the Na_2O_2 precipitate.
21) Only a few milligrams of vanadium were found in the filtrate from P. 51.
22) About twice as much zinc was found in P. 57 as in P. 67
23) Owing to the insolubility of $Zr(OH)PO_4$ it is scarcely possible for zirconium and phosp
ur together in the analysis of the aluminum and iron groups. The zirconium was undo
in dissolving the precipitates obtained in P. 52–65.

Although all possible combinations of small and large quantities o

elements have not been investigated, the test analyses are sufficiently varied to justify general conclusions as to the reliability of the method of separation and detection of the elements.

An examination of these analyses shows that 1 mg. of any of the seven common elements in various combinations with one another and in the presence of the rarer elements was detected in almost all cases, even when the element was associated with a large quantity of other elements. Zinc frequently escaped detection in the analysis of the aluminum group (in P. 57), but was then always found in the analysis of the iron group (in P. 67) when tested for (see T. A. 131–153, 178, 180). One mg. is, however, near the limit of detectability when the elements of the iron group are present in large quantity. Two mg. of chromium were lost in two cases (T. A. 118, 181) owing to the reduction of the chromate; these analyses served to emphasize the necessity of added precautions, which have since been provided for in the directions. One mg. of iron in the presence of a large quantity of manganese would have been overlooked (in T. A. 180) if it had not been tested for in the solution of the chloric acid precipitate, as directed in P. 62. In the case of aluminum, owing to its being contained in the reagent, it was sometimes difficult (see T. A. 116, 117, 119, 131–136, 144–149) to determine with certainty whether or not 1 mg. was present.

It will be seen from T. A. 142–151 and 180 that the presence of much phosphate does not interfere with the detection of 1 mg. of any of the common elements of these groups. It does, however, cause a larger quantity of zinc to be completely precipitated by sodium peroxide (compare T. A. 141 with 142 and 143). It is shown by 144–146, 150, 151 and 180 that 2 mg. of barium and 1 mg. of magnesium are detected in the process, showing that adequate provision is made for the recovery of the alkaline-earth elements when carried down with these groups, through the presence of phosphate.

The analyses with the rarer elements (T. A. 156 to 181) show that the process led to the detection of 1 mg. of each of these and even of 0.5 mg. of beryllium and titanium in all cases except the following: In T. A. 180 zirconium was missed, owing to the simultaneous presence of much phosphate; but, even in the absence of phosphate, 1 mg. is not far from the limit of detectability in a complete analysis. In T. A. 166, 168, 170 and 178 uranium was missed in the usual place (in *P.58*c* and *d*) owing to the fact that it was carried down with aluminum or beryllium in the treatment with dilute $NaHCO_3$ (*P. 58*a*), but T. A. 168 and 170 and a number of special experiments with mixtures of beryllium and uranium show that in such cases uranium can be detected in *P. 58*h*.

CONFIRMATORY EXPERIMENTS AND REFERENCES.

G. D., Section 1: Precipitation of Zinc with Chromium on adding NH_4OH.
g. Zn as $ZnCl_2$ and 100 mg. Cr as $KCr(SO_4)_2$ were dissolved in 4 cc. HCl (
id 96 cc. water; 10 cc. NH_4OH (0.96) were added a little at a time to the
ixture (giving an excess of about 3 cc. NH_4OH); after 3 or 4 minutes the pre
te was filtered off, the filtrate, which had a very faint pink color was heated to
g; and the precipitate that separated (estimated to contain 2 or 3 mg. Cr) wa
red off. H_2S was finally passed into the alkaline filtrate: no precipitate separ
ns showing that the zinc had been completely carried down with the $Cr(OH)_3$.
ecipitates were united and dissolved in HCl, and the solution treated by P. 5
; the zinc was precipitated as ZnS in P. 57.

For the preparation and properties of $ZnCr_2O_4$, see Chancel, *Compt. rend.*, 43
856); Viard, *Bull. de la soc. chim.* (3), 2, 331 (1889).

*Action of NH_4OH and $(NH_4)_2S$ on Nickel Solutions, and Precipitation of Ni
piling the Brown Solution.*—See C. E., P. 51, N. 12.

The Test for Vanadium with H_2S.—See C. E., P. 51a, N. 1.

The Slow Reduction of Vanadic Acid to Hypovanadic Acid by H_2S.—50 mg.
$_2VO_4$ were dissolved in 4 cc. HCl and 100 cc. water; the mixture was satu
th H_2S in the cold. After about 10 mintues the mixture was filtered several
remove the sulphur that had separated, and the blue filtrate was heated to
g: a large precipitate of sulphur separated, showing that reduction was more
higher temperatures. The mixture was filtered and the hot filtrate again
ted with H_2S: a large precipitate of sulphur separated. After 10 minutes the
re was boiled, filtered and again saturated with H_2S: sulphur separated, sho
at the reduction was still incomplete. The treatment of the hot solution with
as repeated, the sulphur filtered off, the mixture was boiled in a casserole to
$_2S$, and 1 g. KI was added: no iodine was liberated, showing that the reducti
rpovanadic acid was complete.—The first experiments were repeated with
NO_3 (1.20) in 100 cc: the results were the same.

Reduction of Vanadic Acid to Hypovanadic Acid by HCl (1.20).—See Gooch
rtis, *Am. J. Sci.* (4) 17, 41 (1904). The reaction is slow in the cold but rap
ating. When a moderate amount of vanadium is present, the reduction is
solutely complete unless a more concentrated HCl solution is used than that obt
evaporating. Compare C. E. *P. 58*d*, N. 1.

Action of NH_4OH on a Hypovanadate.—100 mg. V as Na_3VO_4 were treated with
P. 21 to reduce it to the hypovanadic state; the solution was evaporated to
cc. and made alkaline with NH_4OH: a dirty gray precipitate separated
g. V as Na_3VO_4 were boiled with concentrated HCl (1.20) to reduce the vanad
e mixture was diluted to 100 cc. and made alkaline with NH_4OH: a small
ecipitate, with a greenish shade, separated. Several cc. NH_4OH were a
e precipitate dissolved.

Precipitation of Vanadium in P. 51 or by NH_4OH alone when Iron or Zinc is Pr
500 mg. Fe as $FeSO_4$ and 100 mg. V as Na_3VO_4 were treated with H_2S by
aporated to 40 cc. and treated by P. 51; the filtrate was tested for vanadiu
P. 51*a*: less than 1 mg. V was found.—The experiment was repeated with 50
and 10 mg. V: no vanadium was found in the filtrate.

500 mg. Fe as $FeCl_3$ and 100 mg. V as Na_3VO_4 were dissolved in 40 cc. conta
cc. HCl (1.12), the solution was made alkaline with NH_4OH, and (without a
$(NH_4)_2S$) the mixture was filtered, and the filtrate was tested for vanadium by
a: only a trace of vanadium was found.—The experiment was repeated wit
g. Fe as $FeSO_4$ and 100 mg. V as Na_3VO_4; the mixture was allowed to stand

shaken frequently in order that the iron might be completely precipitated: no vanadium was found in the filtrate.—50 mg. Fe as $FeCl_3$, 15 mg. V as hypovanadic acid and several grams NH_4Cl were dissolved in a little HCl and 100 cc. water; the solution was made alkaline with NH_4OH, and the filtrate was evaporated to dryness, ignited, dissolved in a little NCl and tested for vanadium by P. 51*a*: only a trace of vanadium was found.—Therefore vanadium is almost completely carried down when a three- to fivefold excess of iron is present.

300 mg. Zn as $ZnCl_2$ and 10 mg. V as H_3VO_4 were treated with H_2S by P. 21, evaporated to 30 cc. and treated by P. 51; the filtrate was tested for vanadium by *P. 51*a*: 3 or 4 mg. V were found. The ZnS precipitate was analyzed by the regular procedure: the remainder of the vanadium was found.

Reduction of Vanadic Acid by HI and its Subsequent Behavior with the Group Reagents.—According to Gooch and Curtis (*Am. J. Science* (4) 17, 45, 1904), the first stage of the reduction, that to V_2O_4, took place rapidly in a dilute HI solution, but the second stage, that to V_2O_3, takes place slowly and only in hot concentrated solutions. When a mixture containing 60 mg. V_2O_5, 1 g. KI and an excess of HCl was evaporated to 2 cc., about 97 per cent. of the vanadium was reduced to a salt corresponding to V_2O_3.

In our experiments 1 mg. V as Na_3VO_4 was dissolved in 15 cc. HCl (1.20) in a 50 cc. round bottom flask; 1 g. NH_4I was added, and the mixture was evaporated carefully to 2 or 3 cc., a capillary ebullator tube being used to prevent bumping. The mixture was diluted with 10 cc. water, and NH_4OH (0.96) was added until the solution after shaking smelled distinctly of it: a dark green precipitate formed. A few drops colorless ammonium sulphide were added: the precipitate did not dissolve. It was filtered off and dissolved in a little HNO_3; a large excess (5 to 10 cc.) of NH_4OH (0.90) was added and the mixture saturated with H_2S: the solution became red, showing the presence of vanadium. The filtrate from the NH_4OH precipitate was tested for vanadium in the same way: only a very small amount was found.—The experiment was repeated, except that the evaporated mixture was diluted to 20 cc: more vanadium was found in the filtrate than in the precipitate.—The experiment was repeated, the mixture being diluted to 40 cc.: all the vanadium was found in the filtrate.

The experiment was repeated several times with 100 mg. V, the mixture being diluted to 20 cc. after the evaporation: on adding NH_4OH a dark colored (brown) precipitate separated, but it dissolved completely or in large part on adding a few drops of colorless $(NH_4)_2S$.

The experiment was repeated with 50 mg. V; after the first evaporation 15 cc. HCl (1.20) and 1 g. NH_4I were added, and the evaporation repeated; the mixture was diluted to 50 cc: a large dark greenish colored precipitate separated on the addition of NH_4OH, and it did not dissolve on adding several drops $(NH_4)_2S$. The filtrate was evaporated nearly to dryness; an excess of 5 cc. NH_4OH (0.90) was added, and the mixture saturated with H_2S: not more than 0.5 mg. V was found in the filtrate. The last experiment was repeated with 5 and with 10 mg. V: in the experiment with 5 mg. only a very slight precipitate was obtained on adding NH_4OH and it quickly redissolved; with 10 mg. a precipitate was obtained but about half the vanadium was found in the filtrate. Therefore in a volume of 50 cc. the precipitation is fairly satisfactory for large amounts of vanadium but not for small amounts. The above results were not perfectly reproducible, but each of them was obtained several times.

A number of attempts were made to reduce 50 to 100 mg. V as Na_3VO_4 by evaporating as described above with 10 to 15 cc. pure concentrated HI, and to precipitate

he vanadium with NH_4OH after diluting to 40 or 50 cc.; but the precipitatio
nuch less complete than after the reduction with NH_4I and HCl, probably c
o the larger proportion of iodine found to be retained in the solution in the fo
ase.—The experiments were repeated with HI that had been exposed to the ai
ontained much iodine: the precipitation was still less complete.

Rate of Oxidation of Trivalent Vanadium in the Presence of NH_4OH, and of (NH
–50 mg. V was reduced twice by evaporation with 15 cc. HCl (1.20) and 1 g.
o 2 or 3 cc.; the residue was diluted to 50 cc., and made alkaline with NH
The mixture was divided into two parts; one was filtered at once and the second
alf an hour; both filtrates were tested for vanadium by *P. 51*a*: a very poo
ras obtained in the first filtrate, and a good one in the second. The experimen
epeated, except that the second portion was filtered after 2 hours: the first fi
ave a slight test for vanadium; the second contained 2 to 4 mg. V. Therefo
xidation takes place slowly in the presence of NH_4OH.

The experiments were repeated except that several drops colorless $(NH_4)_2S$
lso added: the filtrates obtained at once, after 1/2 hour, and after 2 hours gave
light tests for vanadium. Therefore the addition of a little $(NH_4)_2S$ does not
he vanadium hydroxide to dissolve, and the rate of oxidation is slower in the
nce of $(NH_4)_2S$ than in that of NH_4OH alone.

The oxidation, by the oxygen of the air of the trivalent vanadium after di
s therefore much too slow to account for the abnormal results, such as the
omplete precipitation of 50 to 100 mg. V in one experiment, and the non-pre
ion in another performed under apparently the same conditions.

G. D., Section 2: Action of HCl on NiS or CoS.—Herz (*Z. anorg. Chem.*, 2
nd 28, 343, 1901) treated sulphides which had been kept on filters for several
after precipitation with 0.5 normal HCl (1 vol. HCl (1.12) and 12 vols. water
ound that the evolution of H_2S could not be detected by odor or by action on
noistened with a lead salt. On the other hand, he found H_2S to be evolved
apidly by the action of 0.5 normal HCl on freshly precipitated sulphides. He
ludes that there are two allotropic forms of the sulphides, one that is soluble
normal HCl, and one that is not. As Glixelli (*Z. anorg. Chem.*, 55, 297, 1907
pointed out, this evidence of decreased solubility is not very conclusive, for t
ction with the old sulphides may simply be much slower. The following experi
how that NiS, at any rate while freshly precipitated, is not a mixture of two sul
liffering markedly in solubility.

200 mg. Ni as NiS, precipitated in the cold by passing H_2S into NH_4OH sol
was digested in the cold for a known time with about 30 cc. dilute HCl (1 vol
1.12) and 5 vol. water). The HCl was first saturated with H_2S, and H_2S was
hrough the mixture in a small flask during the treatment. The mixture was fi
nd the experiment repeated several times with the NiS residue. The amou
nickel dissolved in each treatment was estimated by adding NH_4OH and precipi
he nickel as NiS by passing in H_2S. In the first treatment of 15 min. about 2
Ni dissolved; in each of the next four treatments of 15 min. each, steadily decr
mounts of Ni dissolved, and in the 5th treatment the amount was estimated
0 mg. Ni. The 6th and 7th treatments were each for half an hour: somewhat
nickel dissolved than in the 5th treatment of 15 minutes. The 8th treatmen
or 4 hours: nearly as much dissolved as in the first treatment (say 18 mg.).
night, without passing the current of H_2S, about 20 mg. Ni dissolved. In a last
nent for 6 hours, 25 or 30 mg. dissolved. The final residue contained only
0 mg. Ni.—A similar series of experiments was performed, except that the H
not saturated with H_2S and no H_2S was passed through the mixture: the result

similar, except that the NiS dissolved more slowly owing to the fact that the mixture was very little stirred.

100 mg. Ni as NiS (precipitated by H_2S in NH_4OH solution) were digested with 30 cc. dilute HCl (1 vol. HCl (1.12) and 3 vols. of water) for 5 minutes: about 5 mg. Ni dissolved.—The experiment was repeated with HCl (1.12): the amount of Ni that dissolved was not much greater than in the preceding experiment.—The last experiment was repeated with 1 mg. Ni: only a small proportion of the nickel dissolved.

Action of HCl on NiS when Other Sulphides are also Present.—500 mg. Fe as $FeSO_4$ and 5 mg. Ni as $NiSO_4$ were dissolved in 50 cc. water containing 2 cc. H_2SO_4 (1.84), and the solution treated at about 40° with NH_4OH and $(NH_4)_2S$ as described in P. 51: the filtrate was clear and light colored, showing that it contained no nickel. The precipitate was dried by suction, and treated in a casserole with 30 cc. cold dilute HCl (1 vol. HCl (1.12) and 5 vols. water), with frequent stirring, for 5 minutes: only a very small black residue remained, which was found to contain about 0.5 mg. Fe but no nickel.—The experiment was repeated, except that ferric chloride was used instead of ferrous sulphate: the residue contained 1 or 2 mg. Fe and a mere trace of nickel.—Both experiments were repeated, except that the sulphides were precipitated at about 90° by passing H_2S into NH_4OH solutions. In the experiment with ferrous iron the residue insoluble in dilute HCl contained nearly 1 mg. Fe and less than 1 mg. Ni; in the experiment with ferric iron the residue contained about 1 mg. Fe and nearly all the nickel.—The last experiment was repeated with 500 mg. Fe as $FeCl_3$ and 2 mg. Ni as $NiSO_4$: the residue insoluble in cold dilute HCl contained a little iron and nearly all the nickel.—The first of the above experiments was repeated with 500 mg. Fe as $FeSO_4$ and 10 mg. Ni as $NiSO_4$; the residue insoluble in dilute HCl and also the filtrate were tested for iron and nickel: the residue contained about 1 mg. Fe and 5 mg. Ni; the HCl solution contained also about 5 mg. Ni.—The experiment was repeated except that the sulphides were precipitated at about 90° by passing H_2S into an NH_4OH solution: the residue insoluble in dilute HCl contained about 0.5 mg. Fe and 3 or 4 mg. Ni.

500 mg. Mn as $MnSO_4$ and 5 mg. Ni as $NiSO_4$ were dissolved in 2 cc. H_2SO_4 (1.84) and 50 cc. water, and the solution was treated with NH_4OH and $(NH_4)_2S$ as described in P. 51; the filtrate was clear, showing the absence of nickel. The precipitate was digested with 30 cc. cold dilute HCl (1 vol. HCl (1.12) and 5 vols. water), with frequent stirring, for 5 minutes: the small dark colored residue on analysis was estimated to contain 3 or 4 mg. Ni; the HCl solution contained only about 0.5 mg. Ni.

The experiment was repeated with 500 mg. Zn as $ZnSO_4$ and 2 mg. Ni as $NiSO_4$: after 10 minutes treatment with the dilute HCl a very large residue remained; the HCl solution contained only about 100 mg. Zn, and no Ni. The 2nd treatment with HCl lasted over night: about 300 mg. Zn and no Ni dissolved. The third treatment lasted two days: the residue was small and dark colored, and contained over 1 mg. Ni and little or no Zn; the HCl solution contained about 100 mg. Zn and a little Ni. The experiment was repeated with HCl (1.12): a black residue remained.

These experiments show that small amounts of NiS may be dissolved completely when distributed throughout a large precipitate of iron sulphide, but that they are not readily dissolved in the presence of ZnS or MnS. They also show that ZnS dissolves slowly in dilute HCl just as NiS does.

G. D., Section 6: Precipitation of Vanadium by Alkaline Hydroxides when Uranium is Present.—For the insolubility of uranyl vanadate, see v. Klecki, *Z. anorg. Chem.*, 5, 381 (1894); Carnot, *Compt. rend.*, 104, 1850 (1887); also C. E. *P. 58*a*, N. 3.

50 mg. V as Na_3VO_4 and about 250 mg. U as $UO_2(NO_3)_2$ were dissolved in 3 or 4 cc. HNO_3 (1.20) and 30 cc. water; the solution was made alkaline with NH_4OH (0.96):

a large yellow precipitate separated. This was filtered off and the solution was tested for vanadium by *P. 58*e*: not more than 1 mg. was found. In this experiment there was just sufficient uranium to form $UO_2NH_4VO_4$. The precipitate obtained in the preceding experiment was dissolved in a little HNO_3, diluted to about 15 cc. and poured into about 20 cc. 10 per cent. NaOH solution: a large yellow precipitate separated, This was filtered off and the filtrate tested for vanadium by *P.58*e*: only 5 to 10 mg. V were found.

Separation of Zinc and Vanadium by Hydrogen Sulphide.—H_2S was passed into a solution containing H_3VO_4 and acetic acid: the solution slowly became blue and sulphur separated, which rapidly became dark colored owing to the precipitation of some V_2S_4.

1 mg. V as Na_3VO_4 and 50 mg. Zn as $Zn(NO_3)_2$ were dissolved in 30 cc., a little acetic acid was added, and an excess of about 3 cc. NH_4OH (0.90). The clear solution was saturated with H_2S. A heavy precipitate of ZnS separated at once, and the solution slowly became deep red in color, which color was very distinct after filtering.—The experiment was repeated with 1 mg. Zn and 50 mg. V: a precipitate of ZnS was obtained, which was confirmed by the last paragraph of P. 57.

Action of NH_4OH on Uranium Solutions containing H_2O_2.—100 mg. U as $UO_2(NO_3)_2$ were treated by P. 52. The red (peruranate) solution was made acid with HNO_3. Without heating, the acid solution (which contained H_2O_2, see C. E., P. 52, N. 6) was made alkaline with NH_4OH: a large yellow precipitate of $(NH_4)_2U_2O_7$ separated, but the filtrate was yellow. The filtrate was acidified with HNO_3, boiled for two or three minutes, and again made alkaline with NH_4OH: a large yellow precipitate separated, which was nearly as large as the first NH_4OH precipitate. The colorless filtrate was again acidified, boiled, and then made alkaline with NH_4OH: no precipitate separated. Therefore uranium, if present, will divide in P. 53.

To a nitric acid solution containing 200 mg. U as $UO_2(NO_3)_2$ and 40 mg. V as H_3VO_4 in 40 cc. were added about 20 cc. 3 per cent. H_2O_2; the mixture was made alkaline with NH_4OH: no precipitate separated, showing that the precipitation of $UO_2NH_4VO_4$ and of $(NH_4)_2U_2O_7$ is prevented by the presence of an excess of H_2O_2.

Action of $BaCl_2$ on Uranate Solutions.—100 mg. U as $UO_2(NO_3)_2$ were treated by P. 52 and 53. The yellow filtrate from the NH_4OH precipitate, which contained about half the uranium, was treated by P. 55: a moderately large precipitate separated. After standing over night the precipitate was filtered off and the filtrate tested for uranium by adding HNO_3, boiling and adding NH_4OH: a small yellow precipitate separated, which was estimated to contain 2 mg. U. Therefore barium uranate (or peruranate) may be precipitated nearly completely in P. 55.

Action of $BaCl_2$ on Vanadate Solutions.—100 mg. V as Na_3VO_4 were treated by P. 52 and 53. See C. E., P. 52, N. 10. The NH_4OH solution, which had a volume of about 40 cc., was made just acid with acetic acid and $BaCl_2$ solution was added in the cold as described in P. 55: no precipitate separated from the yellow solution in 5 minutes.—The experiment was repeated with 300 mg. V: no precipitate appeared when the $BaCl_2$ was first added, but in 10 minutes a large orange precipitate of barium vanadate had separated. This was filtered off and the filtrate allowed to stand over night: a large precipitate formed. The precipitate was collected on a filter and washed with water: much of it dissolved, showing that barium vanadate is fairly soluble in water. A portion of the filtrate which was still slightly yellow was tested for vanadium by *P. 58*e*: much vanadium was found, showing that the precipitation of barium vanadates take place slowly, and that large amounts of vanadium remain in the filtrate in the cold.—A solution containing 100 mg. V as Na_3VO_4 and a little NH_4OH in 40 cc. was made acid with acetic acid; 10 cc. 10 per cent. $BaCl_2$ solution were added,

and the mixture was boiled for a minute or two: a large nearly white precipitate separated, and the solution became perfectly colorless. The precipitate was filtered off and the filtrate tested for vanadium by *P. 58*e*: the filtrate was found to contain not more than a few milligrams of vanadium, thus showing that a large proportion of the vanadium had been precipitated on boiling.—The last experiment was repeated except that the acetic acid solution was made alkaline with NH_4OH before boiling: the filtrate was found to be nearly free from vanadium.—The last experiment was repeated with a mixture of 100 mg. V and 10 mg. Zn as nitrate: only about 3 mg. Zn were found in the filtrate, showing that a large part of it had been precipitated with the vanadium, probably as zinc vanadate.

Action of NH_4OH on Solutions containing Zinc and Vanadium as Vanadate.—500 mg. Zn as nitrate and 100 mg. V as Na_3VO_4 were treated by P. 52: only a very small precipitate remained and the solution was colorless. The filtrate was acidified with HNO_3 (1.20), an excess of about 2 cc. being added; and the solution was made just alkaline with NH_4OH: a large precipitate separated. 4 cc. NH_4OH (0.96) were added: the precipitate dissolved completely. The NH_4OH solution was neutralized with acetic acid: a large precipitate separated but it dissolved when a small excess of acetic acid was added. The acetic acid solution was boiled for a minute or two: a large precipitate separated leaving a clear solution, which, however still contained considerable zinc and vanadium.

Separation of Zinc and Uranium by NH_4OH.—1 mg. Zn as $Zn(NO_3)_2$ and 100 mg. U as $UO_2(NO_3)_2$ were dissolved in 4 cc. HNO_3 (1.20) and 100 cc. water; the mixture was made alkaline with NH_4OH and an excess of about 3 cc. added; the yellow precipitate was filtered off and the solution tested for zinc with H_2S: a small nearly white precipitate separated.—The experiment was repeated with 50 mg. Zn and 100 mg. U: the filtrate contained nearly all the zinc. The precipitate was washed, dissolved in HNO_3, diluted to 100 cc. and treated again with NH_4OH: the filtrate contained only about 2 mg. Zn. The NH_4OH precipitate was again treated in the same way: the filtrate contained no zinc.

Action of NH_4OH on Solutions containing Uranium and Chromate.—4 mg. Cr as K_2CrO_4 and 100 mg. U as $UO_2(NO_3)_2$ were treated as described in the preceding paragraph: the filtrate from the NH_4OH precipitate contained nearly all the chromium; the second NH_4OH filtrate was colorless.—The experiment was repeated with 50 mg. Cr and 100 mg. U: the filtrate after the second NH_4OH precipitation was nearly colorless, thus showing that little or no chromium was carried down with the uranium.

G. D., Section 13: The Separation of Titanium and Zirconium by Boiling with Sulphurous Acid.—With regard to the unsatisfactory nature of the process usually employed, see Hillebrand, *Bull. U. S. Geol. Sur.*, 176, 72–3 (1900). A fairly satisfactory quantitative separation of titanium from iron is obtained by boiling a solution of a volume of about one liter containing acetic and sulphuric acids. This large volume is impracticable in qualitative analysis, and H. I. Wood and B. E. Schlesinger (Theses M. I. T. 1901, 1902) devised the following method: "Heat the HCl solution (volume 10 to 20 cc.) to boiling, remove the flame, add at once carefully NH_4OH until litmus paper is turned distinctly blue; add 30 to 40 cc. H_2SO_3 solution, and place on the water-bath for 15 to 20 minutes." This method was carefully tested by us. The results were satisfactory with titanium or zirconium alone, and small quantities of these elements were easily detected. But when iron was also present, some of it was carried down. In an experiment with 3 mg. Fe, 100 mg. Ti and 100 mg. Zr as chlorides, no test for iron was obtained in the filtrate, thus showing that this amount of iron had been completely carried down. Also when 500 mg. alone (as $FeCl_3$) of Fe were present, some of the $Fe(OH)_3$ precipitated by NH_4OH did not dissolve in the H_2SO_3 solu-

on; and even when ferrous iron was used, some $Fe(OH)_3$ sometimes precip
uring the heating on the waterbath. Moreover, the precipitation of titaniu
rconium was usually incomplete when much of these elements were present,
specially if the solution was not made distinctly alkaline with NH_4OH. This m
therefore a very unsatisfactory one.

G. D., Section 17· Precipitation of Beryllium Phosphate as a Confirmatory T
ee B. E. Schlesinger, Thesis, M. I. T. 1902; Classen, Ausgewählte Meth. d. A
hemie, 5th Ed., 1, 715.

1 mg. Be as $BeCl_2$ was in each of three experiments dissolved in water cont
little HCl; 1 cc. 10 per cent. citric acid and 2 cc. 10 per cent. ammonium pho
olutions were added, the mixture was made strongly alkaline with ammonia, and
oiled gently for about 5 minutes in a small flask: a small white crystalline prec
eparated.—The experiment was twice repeated with 2 mg. Al as $AlCl_3$: no prec
eparated.—The experiment was repeated with 0.5 mg Be: no precipitate re
experiments). Therefore this confirmatory test is hardly delicate enough,
ally since beryllium has a very low atomic weight.

Test for Zirconium with Turmeric Paper.—The following procedure recomm
y B. E. Schlesinger (Thesis, M. I. T., 1902) was tested: "Dissolve the pho
recipitate in HF (1: 5), evaporate to one or two drops, and dip a piece of tu
aper into it; heat the paper at 100° until dry" (Pink color, presence of *zirco*
n agreement with the results of Schlesinger, 1 mg. was found to be the limit
etability. Even with 2 mg. the test was not a striking one. Moreover, tit
so caused a pink coloration of the turmeric paper, and the test was more d
han in the case of zirconium. The blank test with strong HF was not perfectly
actory. The results obtained when HCl, instead of HF, was used were prac
he same.

P. 51, N. 2: Precipitation of Small Amounts of Various Elements by Ammo
5 and 1 mg. of Al, Be, U, and Zr as nitrate, of Fe as $FeSO_4$, of Cr as $Cr_2(S$
i as $TiCl_4$ were dissolved in separate experiments in 4 cc. HCl (1.12) and 30 cc.
small conical flasks; the solutions were neutralized with NH_4OH (0.96) and
cc. excess added; the mixtures were shaken several times and then allowed to
few minutes: in each case the solution was transparent after the NH_4OH was
ut a distinct flocculent precipitate was observed after the shaking and sta
he precipitates were more difficult to see with chromium, aluminum, and ur
han with the other substances, but even in these cases 0.5 mg. was easily de
The experiments with aluminum, uranium, and chromium were repeated in a
100 cc. containing 4 cc. HCl (1.12): 1 mg. Al was near the limit of detect
a cold solution, but 0.5 mg. could be easily detected if the solution were
early to boiling and allowed to stand. With uranium the limit of detectabili
to 2 mg. in a cold solution, and with chromium it was 2 mg. in a cold solutio
ith 0.5 mg. Cr the solution became turbid on heating the NH_4OH solution t
g.

2 mg. Cr as $KCr(SO_4)_2$ were dissolved in 4 cc. HCl (1.12) and a little water; th
on was boiled, diluted to 100 cc., cooled, and made alkaline with NH_4OH
very small precipitate was seen after shaking and standing. This was filter
nd the nearly colorless filtrate was heated to boiling: a finely divided, light
recipitate then separated, showing that precipitation of $Cr(OH)_3$ by NH_4OH
old is incomplete.

Solubility of Zinc and Nickelous Hydroxides in Solutions containing NH_4
H_4OH.—To a number of solutions containing 500 mg. Zn as $ZnCl_2$ and va
mounts of HCl in 30 cc. of solution, known amounts of NH_4OH (0.96) were gra

added, 1.0 cc. HCl (1.12) being equivalent to about 1.5 cc. NH_4OH (0.96). The following table shows the amount of NH_4OH that had to be added (1) before a large precipitate was formed, (2) before a distinct odor of NH_4OH persisted after shaking, and (3) before the precipitate dissolved to give a colorless solution.

HCl (1.12) present.	NH_4OH (0.96) required to give a large precipitate.	to give a distinct odor.	to dissolve the precipitate.
2 cc.	3 cc.	8 cc.	11 cc.
4 cc.	7 cc.	11 cc.	14 cc.
6 cc.	11 cc.	14 cc.	16 cc.
8 cc.	no precipitate.	17 cc.	....

The experiment was repeated in a volume of 100 cc. containing 4 cc. HCl (1.12): the result was practically the same as in the corresponding experiment with an initial volume of 30 cc.

The experiments were repeated with 500 mg. Ni as $NiCl_2$, the initial volume being 30 cc.: the solution became blue when an excess of NH_4OH was added, but no precipitate separated even when only 2 cc. HCl were used. In an experiment with no acid, a large green precipitate resulted, which dissolved on adding about 6 cc. excess NH_4OH after the odor of NH_4OH was persistent.

Precipitation of Cobalt Hydroxide.—The foregoing experiments were repeated with 500 mg. $CoCl_2$ and 4 cc. HCl (1.12) in 30 cc.: when the NH_4OH was added slowly a moderately large green precipitate was always obtained, which did not dissolve on adding a large excess of NH_4OH; the supernatant solution was reddish brown. The experiments were repeated with 4 and 6 cc. HCl (1.12), the ammonia (3–4 cc. excess) being added all at once: no precipitate was obtained, but the solution was red colored, and darkened on standing owing to oxidation. The experiments were repeated in a volume of 100 cc. containing 4 cc. HCl (1.12): the results were the same, except that the amount of green precipitate formed was greater than in the smaller volume and that a larger excess of NH_4OH was necessary, in order to prevent the separation of a precipitate when the excess of NH_4OH was added all at once.

Solubility of Aluminum Hydroxide in Excess of Ammonia.—To a solution containing 10 mg. Al as nitrate and 4 cc. HCl (1.12) in 100 cc. were added in the cold 17 cc. NH_4OH (0.96); *i. e.*, an excess of about 10 cc. and the mixture was shaken; the precipitate of $Al(OH)_3$ was filtered off after about five minutes, and the filtrate was boiled for several minutes to expel the excess of NH_4OH: a precipitate of $Al(OH)_3$ separated which was estimated to contain about 3 mg. Al. The experiment was repeated, except that an excess of only 2 or 3 cc. NH_4OH (0.96) was used: the filtrate on boiling became turbid, but the amount of aluminum that separated did not exceed 0.5 mg.

P. 51, N. 3 and 4: Solubility of $Mg(OH)_2$ in NH_4Cl Solutions.—The solubility of $Mg(OH)_2$ in water is about 2×10^{-3} mols. per liter. For evidence that the non-precipitation of $Mg(OH)_2$ in moderately dilute solutions containing an ammonium salt depends solely on the driving back of the dissociation of NH_4OH, see Lovén, *Z. anorg. Chem.*, 11, 404 (1896); Treadwell, *Z. anorg. Chem.*, 37, 326 (1904); Herz and Muhs, *Z. anorg. Chem.*, 38, 138 (1904).

The following experiments show that enough ammonium salt is produced by the neutralization of the 4 cc. HCl (1.12) originally present to prevent the precipitation of $Mg(OH)_2$ even when 500 mg. are present. A solution containing 500 mg. as $MgCl_2$ and 4 cc. HCl (1.12) in 100 cc. was neutralized with NH_4OH (0.96) (6 cc.), and more NH_4OH was added. No precipitate formed when 40 cc. in all had been added, but the addition of 10 cc. more gave a precipitate.—The experiment was repeated with an initial volume of 30 cc. instead of 100 cc.: 30 cc. NH_4OH produced no precipitate,

even after several minutes, but 40 cc. did.—The experiment was repeated with
HCl and a volume of 30 cc.: 15 cc. NH_4OH (0.96) produced no precipitate, but
did.

Complex Zinc Ammonia Cathion.—$Zn(NH_3)_4^{++}$. See Herz, *Z. anorg. Che*
225 (1900); Gaus, *Z. anorg. Chem.*, 25, 236 (1900); Euler, *Ber.*, 36, 3400 (1903);
dorff, *Z. anorg. Chem.*, 41, 132 (1904).

Complex Nickel Ammonia Cathion.—$Ni(NH_3)_4^{++}$. See Dawson and McC
Chem. Soc., 77, 1239 (1900); Konowaloff, *Chem. Centralblatt*, 1900 I, 646; and
cially Bonsdorff, *Z. anorg. Chem.*, 41, 132 (1904).

Behavior of Chromium towards Ammonium Hydroxide.—To a solution con
in 30 cc. 3 or 4 cc. HCl (1.12) and 250 mg. Cr as $CrCl_3$ freshly prepared by boiling
with concentrated HCl, was added NH_4OH (0.96) until after shaking the od
distinct. The mixture was divided into two parts; one part was filtered a
to the other part 10 cc. NH_4OH (0.96) were added, and it was immediately f
the former had only a very faint pink color, and on boiling not more than c
Cr precipitated as $Cr(OH)_3$; the latter was distinctly pink, and on boiling 2 to
Cr precipitated as $Cr(OH)_3$.—The experiment was repeated, except that an
of 2 cc. NH_4OH was added after the odor of NH_4OH was distinct, and that i
tion 5 g. solid NH_4Cl were added to one-half of the mixture, and both portio
filtered at once: each filtrate was faintly pink, and on boiling that containing
cess of NH_4Cl there resulted a precipitate of $Cr(OH)_3$ estimated to contain
Cr, while on boiling the other filtrate no precipitate separated, and the solu
mained pink.—The last experiment was repeated, except that the mixtures w
lowed to stand 20 hours before filtering: the filtrate containing no excess of
was faintly pink but did not contain more than 1 mg. Cr. The second filtra
highly colored and on boiling 5 to 10 mg. Cr precipitated as $Cr(OH)_3$, but the
tation was not quite complete. These results show that both NH_4OH and
increase the amount of the pink chromium compound formed, and therefore
that this compound is a complex ammonia salt and not a chromite. For th
that these solutions are unstable, even at room temperatures, see Herz, *Z.*
Chem., 31, 357 (1902).

P. 51, N. 6: Precipitation of Phosphates of Calcium, Barium, Magnesium and
nese by Ammonium Hydroxide.—To solutions containing 2 mg. PO_4 as Na_2HP
4 cc. HCl (1.12) in 30 cc., were added in separate experiments varying amo
manganese, barium, and magnesium, as chloride and of calcium as nitrat
solutions were then neutralized with NH_4OH (0.96) and about 2 cc. excess
making 8 cc. in all, after which the mixtures were shaken and allowed to s
and 3 mg. Mn gave small precipitates after a minute or two, but 1 mg. gave
cipitate; 10 and 20 mg. Ca gave large precipitates at once but 5 mg. gave no
tate even in half an hour. 100 mg. Ba gave a large precipitate at once, and
gave no precipitate in half an hour. 1, 3 and 5 mg. Mg. gave precipitates on s
—The experiment was repeated with 10 mg. PO_4 and varying amounts of bariu
mg. Ba gave a large precipitate at once, but 40 mg. gave no precipitate, or
very small one, in half an hour.—The experiment was repeated with 2 mg. Ca an
ing amounts of phosphate: with 30 mg. PO_4 a precipitate was obtained at onc
20 mg. after several minutes, and with 10 mg. no precipitate appeared in half a
On repeating the experiment with 1 mg. Ca a precipitate was obtained with
PO_4 after a few minutes but not with 20 mg.

P. 51, N. 7: Solubility of the Borates of the Alkaline Earth Element
mg. BO_3 as H_3BO_3 and 20 mg. Ca as chloride were dissolved in 4 cc. HCl (1.1
36 cc. water, and NH_4OH (0.96) were added until the mixture after shakin

smelled of it: no precipitate separated.—The experiment was repeated with 200 mg. Ba as chloride; no precipitate separated.—The experiment was repeated with 300 mg. Ba; a small precipitate formed, but it dissolved on adding a little concentrated NH_4Cl solution.—The experiment was repeated with 500 mg. Mg as chloride: no precipitate resulted.

P. 51, N. 9: Action of Ammonium Hydroxide on Uranyl Solutions.—See Kern. *J. Am Chem. Soc.*, 23, 701–5 (1901).—1 and 3 mg. U as $UO_2(NO_3)_2$ were dissolved in separate experiments in 20 cc. water, and a few drops NH_4OH (0.96) were added: no precipitate separated on standing, nor on boiling. A small quantity of solid $NaNO_3$ was added to the cold solutions: pale yellow precipitates separated at once, showing that the uranium had been present in the colloidal form.—The experiment with 1 mg. U was repeated, except that a little NH_4Cl instead of $NaNO_3$ was added: a yellow precipitate separated.

P. 51, N. 9: Uranyl Salts and Diuranates.—See Dittrick, *Z. physik. Chem.*, 29, 449–90 (1899); Kern, *J. Am. Chem. Soc.*, 23, 686–726 (1901).

P. 51, N. 10: Completeness of Precipitation of the Sulphides of the Iron Group.—In each of the following experiments the quantity of the element given below was dissolved in 4 cc. HCl (1.12) and 96 cc. water; to this solution in the cold were added 9–10 cc. NH_4OH (0.96), and then $(NH_4)_2S$ solution drop by drop until an excess was present. The mixtures were well shaken and then filtered, generally through a double filter. The results were as follows: With 5 mg. Mn as $MnCl_2$, a light colored precipitate was formed at once; the filtrate was clear after two filtrations. With 0.5 mg. Mn as $MnCl_2$, the result was the same. With 0.25 mg. Mn as $MnCl_2$, the solution became turbid in two or three minutes. The filtrate in the first two experiments was evaporated almost to dryness; HNO_3 (1.42) was added; the mixture was evaporated to 5 cc., $KClO_3$ was added, and the mixture boiled: no precipitate of MnO_2 separated, showing that the precipitation of MnS had been complete.

With 1 mg. Zn as $Zn(NO_3)_2$, the mixture became turbid at once, and was readily filtered. With 0.5 mg. Zn, the result was the same. The filtrate in the first experiment was evaporated to 5 cc., made alkaline with NH_4OH and $(NH_4)_2S$ was added: only an insignificant turbidity appeared, showing that the precipitation of ZnS was practically complete.

With 0.5 mg. Co as $Co(NO_3)_2$, a black precipitate formed at once, which was readily filtered off. With 0.1 mg. Co, the solution became dark colored at once.

With 0.2 mg. Fe as $FeSO_4$, the solution became dark colored at once and the precipitate was easily filtered off. With 0.5 mg. Fe as $FeSO_4$, the result was the same. The filtrate was evaporated to 5 cc.; NH_4OH and $(NH_4)_2S$ were added: the solution remained colorless.

With 0.3, 0.5 and 1.0 mg. Tl as Tl_2SO_4, the solutions became dark brown at once and yielded clear filtrates, which when evaporated almost to dryness and tested for thallium by *P. 65*d*, gave no precipitate of TlI.

With 0.5 and 1.0 mg. U as $UO_2(NO_3)_2$, distinct flocculent precipitates could be seen after the addition of $(NH_4)_2S$; the filtrates were clear, and the precipitate, when collected on the filter, was yellow in color. With 0.3 mg. U as $UO_2(NO_3)_2$, a slight coloration was seen on the filter, but the precipitate could scarcely be seen before filtration. With 5 mg. U as $UO_2(NO_3)_2$, the result was the same. The filtrate was evaporated almost to dryness, and was tested for uranium by *P. 58*d* with $K_4Fe(CN)_6$: no brown coloration was observed. The last experiment was repeated except that the filtrate was evaporated to 5 cc. and NH_4OH and $(NH_4)_2S$ added: no precipitate formed, showing that the precipitation as sulphide in 100 cc. had been complete.

Nature of the Uranium Precipitate Produced by Ammonium Sulphide.—20 mg. U

as $UO_2(NO_3)_2$ were dissolved in 4 cc. HCl (1.12) and 96 cc. water, about 9 cc. NH_4OH were added and $(NH_4)_2S$ drop by drop in the cold, until a distinct excess was present. The precipitate was flocculent and had a bright yellow color. After two hours it was light brown and in six hours dark brown in color.—The experiment was repeated except that a much larger excess of $(NH_4)_2S$ was added: the precipitate darkened more rapidly. It is evident that $(NH_4)_2U_2O_7$ is first precipitated contrary to the statements in some text books, and that the conversion of this substance into UO_2S takes place slowly.

The Existence of Ferric Sulphide (Fe_2S_3).—That Fe_2S_3 is formed when $(NH_4)_2S$ is added to suspension of $Fe(OH)_3$ in dilute NH_4OH has been proved by Stokes, *J. Am. Chem. Soc.*, **29**, 304 (1907). When, however, an acid solution is first saturated with H_2S and then made alkaline with NH_4OH, FeS and not Fe_2S_3 is formed.

P. 51, N. 11: Dark Color of Sulphide Precipitate as Evidence of Iron, Nickel, or Cobalt.—To solutions containing 500 mg. Zn as nitrate, 4 cc. HCl (1.12) and 30 cc. H_2O were added in separate experiments 1 and 2 mg. Ni as nitrate, 1 and 2 mg. Co as nitrate, 1 mg. Fe as $FeSO_4$ and 1 mg. Fe as $FeCl_3$. The mixtures were neutralized with NH_4OH (0.96) and 3 or 4 cc. excess added, making 10 cc. in all: A large white precipitate of $Zn(OH)_2$ remained which was estimated to contain at least 100 mg. Zn. Colorless $(NH_4)_2S$ was then added as described in P. 51 and the color of the precipitates was compared with that obtained with 500 mg. pure zinc; the precipitates containing 1 mg. Fe were nearly black with a greenish tinge; those containing 2 mg. Ni and Co were much darker than the pure ZnS, but those with 1 mg. Ni and Co were only very slightly darker.—The experiments were repeated except that 4 cc. more NH_4OH were added in order to dissolve the $Zn(OH)_2$: the results were substantially the same.--A solution containing 500 mg. Ca and 1 mg. Ni as nitrates, 1 g. PO_4 as $(NH_4)_2HPO_4$, 4 cc. HCl (1.12) and 35 cc. H_2O was made alkaline with NH_4OH (0.96) and 1 cc. colorless $(NH_4)_2S$ was added: the large white precipitate of phosphate became dark colored as soon as the sulphide was added.

P. 51, N. 12: Behavior of Nickel towards Ammonium Monosulphide and Polysulphide.—See Lecrenier, *Chem. Ztg.*, **13**, 431, 449 (1889); Anthony and Magri, *Gazz. chim. ital.*, **31**, II, 265 (1901). By boiling the brown solution in the absence of air the last-named authors have prepared NiS_4. The composition of the brown solution is unknown; it may be ammonium sulpho-nickelate, $(NH_4)_2NiS_{2+x}$, or colloidal nickel persulphide.

That in absence of air nickel is completely precipitated as NiS and the filtrate is colorless, thus proving that the brown solution is due to the presence of polysulphide, has been shown by Lecrenier, *Chem.-Ztg.*, **13**, 431, 449 (1889) and Villiers, *Compt. rend.*, **119**, 1263 (1894). The presence of NH_4OH tends to prevent the precipitation of NiS, and it is possible to obtain colorless (or bluish) solutions, containing a small excess both of $(NH_4)_2S$ and of nickel. In the presence of air we have found it almost impossible, when working with large amounts of a pure nickel salt, to prevent some nickel from passing into the filtrate, giving a brown solution. The amount of nickel in the filtrate increased with the excess of ammonium sulphide used and with the length of exposure to the air.

Some of the brown solutions obtained in these experiments were boiled in small flasks for 3 to 10 minutes, and then filtered: in each case the filtrate was colorless after a single filtration.

Precipitation of Nickel in Ammoniacal Solution by Hydrogen Sulphide.—In several experiments 500 mg. Ni as $Ni(NO_3)_2$ were dissolved in 30 cc. water and 4 cc. HCl (1.12); NH_4OH (0.96) was added until the odor could be detected after shaking and then 3 cc. more, and H_2S was led into the mixture for 15 minutes: the precipitates were al-

ways granular, and the filtrates clear and colorless; when the precipitates were washed with water containing either H_2S or a little $(NH_4)_2S$ the wash water was invariably clear.

**P. 51a, N. 1: Test for Vanadate with H_2S in Alkaline Solution.*—To separate solutions containng 3 g. NH_4Cl and 5 cc. NH_4OH (0.90) in a volume of 110 cc. were added 0.1, 0.3 and 0.5 mg. V as vanadate, and the mixtures were saturated with H_2S: in the experiments with 0.3 and 0.5 mg. V the solutions quickly became dark yellow, then reddish yellow and finally pink; in that with 0.1 mg. V the solution finally became faintly pink, but the test was a poor one. Therefore, the limit of detectability under these conditions is 0.1 to 0.2 mg.

The experiment with 0.5 mg. V was repeated except that, instead of 5 cc. NH_4OH (0.90) 1, 2.5 and 10 cc. respectively were used: with 1 cc. and with 2.5 cc. NH_4OH the pink color was scarcely noticeable; with 10 cc. a good color was obtained as with 5 cc. NH_4OH, but only after passing in H_2S for a longer time. These experiments show that a fairly large excess of NH_4OH is necessary.

20 mg. V as Na_3VO_4 were added to 20 cc. NH_4OH (0.96) and H_2S passed in: the color quickly became brown and slowly turned red, becoming after 5 or 6 minutes a deep cherry-red. The solution was divided into two parts. To the first was added an equal volume of water: the red color disappeared in 2 or 3 minutes, but appeared again on resaturating with H_2S. To the second part of the red solution was added an equal volume of NH_4OH (0.96): the color faded slowly (in 4 or 5 minutes) but reappeared on passing in H_2S. These experiments show that the solution must be saturated with H_2S.

1 mg. V as Na_3VO_4 was dissolved (*a*) in 20 cc. NH_4OH (0.90), (*b*) in 20 cc. NH_4OH (0.96), (*c*) in 5 cc. NH_4OH (0.96) and 15 cc. water, (*d*) in 2 cc. NH_4OH (0.96) and 38 cc. water, (*e*) in 2 cc. NH_4OH (0.96) and 98 cc. water. Each solution was saturated with H_2S: a good color was obtained in every case, showing that in the absence of ammonium salts the test may be obtained in any concentration of NH_4OH.

A solution containing 1 mg. V as Na_3VO_4 and 3 cc. HNO_3 (1.42) in 10 cc. was neutralized with NH_4OH (0.90) and 1 or 2 cc. in excess added: on saturating with H_2S a very faint color was obtained.—The experiment was repeated, except that the acid solution was first evaporated to dryness and ignited: a very good test was obtained, showing that the presence of ammonium salts interferes with test for vanadium.

0.5 mg. V as Na_3VO_4 was added to some HCl (1.20) and the mixture was evaporated twice nearly to dryness to reduce the vanadic acid to hypovanadic acid; 4 cc. HCl (1.12) were added and 96 cc. water; the mixture was neutralized with NH_4OH (0.90), an excess of 5 cc. was added, and H_2S passed in for 10 to 15 minutes: the solution darkened quickly, became reddish yellow and finally pink; the color was exactly the same as in the experiment described above with 0.5 mg. V as Na_3VO_4.—The experiment was repeated with 25 mg. V, which was reduced to hypovanadic acid by long continued treatment of the hot solution with H_2S: the solution darkened and then became deep red very quickly; the color was the same as in the experiment described above with 50 mg. V as Na_3VO_4.

1 mg. V as Na_3VO_4 was dissolved in 18 cc. water, 2 cc. 10 per cent. NaOH solution were added, and the mixture saturated with H_2S: a deep red color was finally obtained which was almost the same as that obtained when NH_4OH was used. The experiment was repeated with 20 cc. undiluted NaOH solution: the final color was the same, but the solution remained colorless for a long time while the H_2S was being passed through it. Therefore the formation of the red compound does not depend on the presence of NH_4OH or NH_4^+ ion.

**P. 51a, N. 2: Action of Acids on Sulphovanadate.*—0.5 mg. V as sodium vanadate

was dissolved in 100 cc. containing about 3 g. NH_4Cl; 5 cc. NH_4OH (0.90) were added, and the mixture saturated with H_2S; the pink solution was filtered, and then acidified in the cold with acetic acid, stirred, and filtered: a small black precipitate containing sulphur was obtained. This was dissolved by boiling with a little HNO_3 (1.20); the solutions were evaporated to about 2 cc. and 1 to 2 cc. 3 per cent. H_2O_2 were added: an orange-yellow color resulted, showing the presence of a small amount of vanadium. —The experiment was repeated with sodium hypovanadate: the results were the same.

The experiment was repeated with 25 mg. V: on boiling the filtrate from the precipitate of vanadium sulphide it became blue and sulphur separated. To it 50 mg. Fe as $FeCl_3$ were added and then an excess of NH_4OH; the mixture was filtered, the filtrate was evaporated to dryness, the residue ignited and dissolved in a very little HNO_3, and a few drops H_2O_2 solution were added: no color appeared, showing that the vanadium in excess of 0.1 mg. had been carried down with the $Fe(OH)_3$. The sulphide and hydroxide precipitates were dissolved separately in HNO_3, H_2O_2 was added together with and 20 to 30 cc. water, and the intensities of the colors compared: it was estimated that about 10 mg. V were precipitated as sulphide, and the remaining 15 mg. V with the $Fe(OH)_3$.—The experiment was repeated with 50 mg. V, a larger amount of $FeCl_3$ being used: the results were similar, thus showing that under these conditions less than half the vanadium is precipitated as sulphide. —In other experiments in which the volume was only 20 to 30 cc., and the relative proportion of ammonium salt to NH_4OH was smaller, 80 to 90 per cent. of the vanadium was found to be precipitated as sulphide by acetic acid. Even when NaOH was used instead of NH_4OH, it was not possible to precipitate the sulphide completely.

The experiment with 50 mg. V described in the last paragraph was repeated, except that HCl was used to acidify the cold solution: it was estimated that roughly one-half of the vanadium was precipitated as sulphide and the other half with the $Fe(OH)_3$. —The last experiment was repeated, except that the mixture containing HCl was boiled for about 1 minute: somewhat less than half the vanadium was found in the HCl precipitate.

**P. 51a, N. 3: Complete Precipitation of Vanadium by Ammonium Hydroxide in the Presence of Iron.*—See preceding section, and C. E., G. D., Section 1.

P. 51a, N. 4: Pervanadic Acid.*—See Scheuer, *Z. anorg. Chem.*, **16, 284 (1898); Pissarjewsky, *Z. phys. Chem.*, **43**, 171 and 173 (1903), and **40**, 368 (1902).

Action of H_2O_2 on Vanadic Acid.—In a series of 6 test tubes, each of which contained 1 mg. V as Na_3VO_4, were placed 0, 0.5, 2, 5, 10, and 20 cc. H_2SO_4 (1.20); each solution was diluted to 20 cc. and 2 cc. 3 per cent. H_2O_2 added: no change was observed in the tube with no acid; the solution became orange to orange-red in the remaining tubes, and the intensity of the color increased greatly as the concentration of the acid increased. The experiments were repeated with HNO_3 (1.20): the results were the same. All the tubes were allowed to stand over night: no changes in the colors were observed. Ether was added to a number of the solutions and the mixtures shaken: the ether layer remained colorless.

To solutions containing 1 mg. V as Na_3VO_4 dissolved in 1 cc. HNO_3 (1.20) were added, (*a*) 1 cc. 3 per cent. H_2O_2 and 8 cc. water, (*b*) 3 cc. H_2O_2 and 6 cc. water, and (*c*) 9 cc. H_2O_2: the first two solutions were orange-red, but the third solution was practically colorless, thus showing that a large excess of H_2O_2 spoils the test. To the third solution were added 3 cc. HNO_3 (1.20): the orange-red color reappeared, thus proving again that the test is more easily obtained in the presence of a large excess of acid. To this solution was then added 7 cc. H_2O_2: the color became much fainter.

The first series of experiments with varying amounts of HNO_3 (1.20) and a total volume of 20 cc. was repeated, except that 0.1 mg. V as Na_3VO_4 was used instead

of 1 mg.: all the solutions remained colorless, showing that 0.1 mg. V cannot be detected in 20 cc.—This series of experiments was repeated with 0.3 mg. V: a distinct yellow color could be seen on looking down the tubes in the experiments with 5, 10, and 20 cc. HNO_3, a light color with 2 cc. HNO_3, and none with 0.5 cc.—This series was repeated with 0.5 mg. V: with 0.5 cc. HNO_3, the solution was colorless, with 2 cc. it was slightly yellow, and in the remaining experiments a slight but distinct orange-yellow color was observed. Therefore the limit of detectability of vanadium with H_2O_2 in HNO_3 solution is about 0.5 mg. V in 20 cc., and the solution must contain at least 1 volume HNO_3 (1.20) to 3 volumes of water.

*P. 51a, N. 5: *Tungstic Acid Dissolves in Acids when Phosphate or Arsenate is Present.—Tech. Quart.*, 16, 122 (1903).

Partial Precipitation of Tungsten on Acidifying a Solution of Sulphotungstate.—See *Tech. Quart.*, 17, 253–5 (1904).

Action of H_2S on Tungstate Dissolved in Excess of NH_4OH.—50 mg. W as $(NH_4)_2WO_4$ and 3 g. NH_4Cl were dissolved in 100 cc. water, 5 cc. NH_4OH (0.90) were added, and the mixture was saturated with H_2S: the solutions remained nearly colorless for over 10 minutes, but finally became slightly yellow, probably owing to the formation of polysulphide.

Action of H_2O_2 on Tungstic and Molybdic Acids.—See *Tech. Quart.*, 17, 251 (1904). —20 mg. Mo as $(NH_4)_2MoO_4$ were dissolved in 5 cc. HNO_3 (1.20) and 2 cc. H_2O_2 added: a lemon-yellow color resulted. On account of the absence of an orange tint there is no difficulty in distinguishing between this color and that of pervanadic acid.

Action of H_2S on Molybdate Dissolved in Excess of NH_4OH.—A solution containing 6 mg. Mo as $(NH_4)_2MoO_4$ and 4 cc. HCl (1.12) in 30 cc. was treated by P. 51: no precipitate formed with NH_4OH, nor with $(NH_4)_2S$. To the nearly colorless filtrate were added 5 cc. NH_4OH (0.90), and H_2S was led through the solution in a test tube for 20 minutes: after 3 minutes the solution was dark yellow, after 5 minutes it had a reddish color, after 10 minutes it was brilliant red, and the color did not change in the next 10 minutes. The color was not the same as in the case of vanadium, but might be mistaken for it if a comparative test were not made.—50 mg. Mo as $(NH_4)_2MoO_4$ and 3 g. NH_4Cl were dissolved in 100 cc. water, 5 cc. NH_4OH (0.90) were added, and the solution was saturated with H_2S: the colors obtained were the same as in the preceding experiment.—The last experiment was repeated with 1 mg. Mo: the solution finally became deep orange in color.

Action of Acids on Sulphomolybdate.—50 mg. Mo as $(NH_4)_2MoO_4$, 3 g. NH_4Cl, and 5 cc. NH_4OH (0.90) were dissolved in 100 cc. water, and saturated with H_2S. The red solution was filtered and then made distinctly acid with acetic acid: the color remained nearly the same; on filtering, a very small black precipitate was obtained which contained less than 1 mg. Mo. The solution was allowed to stand for one hour: it remained clear. After 3 hours a small precipitate had separated which contained only 2 or 3 mg. Mo. The mixture was then boiled for 5 minutes and filtered: about 2/3 of the molybdenum precipitated as MoS_3 and the filtrate was still deep orange. The filtrate was evaporated to a small volume and 10 cc. HCl (1.20) added: a large black precipitate of MoS_3 separated, but the solution was found to still contain 1 or 2 mg. Mo.

The foregoing experiment was repeated, except that HCl was added to the cold solution: a large black precipitate separated at once. The filtrate was evaporated to 30 cc. and tested for Mo by *P. 43e: none was found.—The experiment was repeated except that the mixture was boiled after adding HCl: the result was the same, not more than a trace of molybdenum being found in the filtrate.

P. 52, N. 3: The Formation of Sulphate on Dissolving NiS in Acids.—In two experi-

ments 300 mg. Ni as freshly precipitated NiS were treated by P. 52, the sulphur was filtered off, and $BaCl_2$ was added to the filtrate: small precipitates of $BaSO_4$ separated, each of which was estimated to contain 5–10 mg. Ba.—In another series of experiments the NiS was first treated in the cold for several minutes with mixtures of 5 cc. HNO_3 (1.20) with 20 to 20 cc. water and the residue was dissolved by evaporating the solution to concentrate the HNO_3, and then adding a few drops HCl (1.20): precipitates of $BaSO_4$ resulted, estimated to contain 20–50 mg. Ba. In each of these experiments and especially when the precipitate was first treated with HNO_3 considerable sulphur separated and the NiS enclosed in it did not dissoive readily.

P. 52, N. 4: Action of HCl on Titanium and Zirconium Hydroxides.—Acid solutions containing 100 mg. Ti and 100 mg. Zr as chlorides in volumes of about 100 cc. were treated in the cold with NH_4OH; the precipitates were filtered off and treated with 20 cc. cold HCl (1.12): they dissolved completely in a minute or two.—The experiments were repeated, except that the solutions were heated to boiling, and the NH_4OH was added to the hot solutions: on pouring 20 cc. HCl (1.12) repeatedly through the filters containing the hydroxide precipitates, almost all of the $TiO(OH)_2$ dissolved, but only a small portion of the $ZrO(OH)_2$ (8–10 mg. Zr). On pouring a 20 cc. portion of hot HCl (1.12) repeatedly through the filters, the remainder of the titanium, but only about half the zirconium dissolved. The remainder of the $ZrO(OH)_2$ was boiled in a casserole with HCl (1.12) for several minutes: it dissolved completely.

P. 52, N. 5: Complete Precipitation of Titanium and Zirconium in the Sodium Peroxide Procedure.—1 mg. Ti as $TiCl_4$ was treated with NaOH and Na_2O_2 by P. 52, the mixture being boiled for about 4 minutes after the Na_2O_2 was added: a white precipitate separated. The filtrate was made acid with HCl; one-half of it was tested for titanium by adding H_2O_2: no color appeared, showing that the titanium had been completely precipitated. The other half of the filtrate was tested for H_2O_2 by adding excess of $TiCl_4$: no color appeared, showing that the Na_2O_2 had been completely decomposed.—The experiment was repeated with 500 mg. Ti: the filtrate contained 1 or 2 mg. Ti. The precipitate was treated with HCl (1.12): nearly all dissolved in the cold and the remainder on warming. The solution was reddish yellow, showing that the precipitate contained some TiO_3.—The HCl solution obtained in the last experiment (containing nearly 500 mg. Ti) was treated with NaOH and Na_2O_2 by P. 52; the mixture containing Na_2O_2 was boiled for less than 1 minute: the filtrate contaned at least 5 mg. Ti.—These experiments show that the amount of titanium that remains in the filtrate may be greatly lessened by long continued boiling.

1 mg. Zr as $ZrCl_4$ was treated with NaOH and Na_2O_2 by P. 52: a distinct precipitate separated.—The experiment was repeated with 100 mg. Zr; the large precipitate was filtered off, and the filtrate was tested for zirconium by acidifying with HNO_3, evaporating almost to dryness, and adding Na_2HPO_4 solution: only a trifling precipitate separated, thus proving that the precipitation of the zirconium had been complete.

Action of NaOH on Uranyl Salts.—A solution containing 5 mg. U as UO_2Cl_2 and a little HCl in 15 cc. was neutralized with 10 per cent. NaOH solution, and an excess of 2 or 3 cc. was added: a small yellowish precipitate separated. This was filtered off and the filtrate was tested for uranium by acidifying and adding NH_4OH: a small precipitate separated, which was estimated to contain 2 or 3 mg. U. The experiment was repeated, except that the mixture containing NaOH was boiled for a minute or two: nearly all of the precipitate which had formed in the cold was redissolved. Therefore the uranium is not completely precipitated by a small excess of NaOH.—50 mg. U as $UO_2(NO_3)_2$ were added to 30 cc. 10 per cent. NaOH solution, and the mixture was heated to boiling, cooled, and poured through a hardened filter;

half of the filtrate was tested for uranium as above: only a small precipitate of $(NH_4)_2U_2O_7$ separated, showing that the uranium had been nearly completely precipitated by the alkali.

Composition of Sodium Aluminate, Zincate, Beryllate and Chromite.—For the evidence that sodium aluminate in solution has the formula, $Na^{\cdot}AlO_2^{-}$, see Noyes and Whitney, *Z. physik. Chem.*, **15**, 694 (1894); Hantzsch, *Z. anorg. Chem.*, **30**, 296 (1902). Hantzsch has shown by means of conductivity measurements that a solution of the empirical composition Na_3AlO_3 contains mainly NaOH and $NaAlO_2$ and some colloidal $Al(OH)_3$.

Hantzsch, *Z. anorg. Chem.*, **30**, 298, 303 (1902), concluded from conductivity measurements that a 1/200 molal solution of sodium zincate, even in the presence of a sevenfold excess of NaOH, is almost completely hydrolyzed into NaOH and $Zn(OH)_2$ and that the latter is present as a colloid. Fisher and Herz, *Z. anorg. Chem.*, **31**, 355 (1902), confirmed this by dialysis experiments. Kunchert, *Z. anorg. Chem.*, **41**, 343–8 (1904), working with a larger excess of alkali, and using Bodländer's electromotive force method, proved, however, that the solutions contained chiefly $ZnO_2^{=}$ and some $HZnO_2^{-}$. Förster (*Z. Elektrochem.*, **6**, 301, 1899) has prepared solid $NaHZnO_2$.

Hantzsch (*Loc. cit.*) concludes that H_2BeO_2 is a very weak acid, weaker than $HAlO_2$, but much stronger than H_2ZnO_2.

From dialysis and conductivity experiments Fisher and Herz (*Loc. cit.*) conclude that in alkaline chromite solutions chromium is present almost solely as colloidal $Cr(OH)_3$.

Behavior of Cobalt Hydroxide towards NaOH.—See Donath, *Z. analyt. Chem.*, **40**, 137 (1901).—An acid solution containing 100 mg. Co as nitrate in 30 cc. was neutralized with 10 per cent. NaOH and an excess of 15 cc. added; 2 g. Na_2O_2 were added a little at a time to the cold solution, the mixture was boiled for two or three minutes, cooled, and filtered: the filtrate had a deep blue color. It was acidified, made alkaline with NH_4OH, and H_2S was passed into it: a precipitate separated which was estimated to contain 5 to 8 mg. Co.—The experiment was repeated, except that no excess of NaOH was added: the filtrate was colorless and no cobalt was found in it.—This last experiment was repeated except that 4.5 g. Na_2O_2 were used instead of 2 g.: again the filtrate contained no cobalt. Therefore the blue (soluble) cobalt compound is formed only by the action of concentrated alkali on a *cobaltous* salt, and the cobalt is completely precipitated if it is first oxidized to the cobaltic state by Na_2O_2 in a weakly alkaline solution.

The first experiment with the large excess of NaOH was repeated with 100 mg. Ni instead of Co: no nickel was found in the filtrate.

P. 52, N. 6: Formation of Peruranates. See P. Melikow and L. Pissarschewsky, *Z. physik. chem.*, **28**, 556 (1899). A large number of salts are known in the solid state; *e. g.*, $UO_4.2Na_2O_2.8H_2O$; $UO_4.2BaO_2.8H_2O$; $UO_4.2BaO_2.10H_2O$; etc. The salts of the alkali elements are soluble in water, the others insoluble. These salts may be regarded as compounds of peruranic anhydride, UO_4, with peroxides of the other elements. They were prepared by the action of H_2O_2 on solutions of uranyl salts in the presence of the hydroxides of the other elements.

A HNO_3 solution containing 100 mg. U as $UO_2(NO_3)_2$ in 25 cc. was treated by P. 52: the solution was yellow when acid, and a yellow precipitate separated on adding NaOH; on adding Na_2O_2 (3 g.) and boiling, a deep red solution resulted. This solution was acidified with HNO_3: it became yellow. To a portion of it was added a little $TiCl_4$ in HCl solution: an orange-red color resulted, proving the presence of free H_2O_2. Therefore the uranium is oxidized by Na_2O_2 to a soluble "peruranate," which is stable in the strong alkali, but apparently decomposes readily in the acid solution with forma-

ion of H_2O_2 and a uranyl salt.—The experiment was repeated except that only
).5 g. Na_2O_2 was added a yellow uranium precipitate remained, but the solutio
ained a large proportion of the uranium.

P. 52, N. 7: Complete Decomposition of Na_2O_2 by Boiling.—2 g. Na_2O_2 were
o a neutral solution containing 0.5 g. NaCl in 30 cc., the mixture was heated t
ng, boiled for one minute, cooled, acidified with HNO_3, and tested with $TiCl_4$ s
or H_2O_2; the solution remained colorless.—The experiment was repeated wi
ng. Mn as $MnCl_2$, the MnO_2 being filtered off before the filtrate was made acid:
ained no H_2O_2.—The experiment was repeated with 100 mg. V as Na_3VO_4: the
was the same. See the preceding paragraph as to the effect of uranium

Precipitation of Thallium by Sodium Peroxide.—1, 3, and 20 mg. Tl as T
were treated in separate experiments by P. 52: brown precipitates separated
ase on adding NaOH, and remained after the treatment with Na_2O_2. The so
which were filtered off almost immediately after diluting, were found to contain
).5, 1, and 2 to 3 mg. respectively.—1 mg. Tl as Tl_2SO_4 was treated by P. 52:
ipitate separated on adding NaOH; there was a slight coloration on adding
ut no precipitate remained upon boiling; when, however, the solution was se
o cool, a good precipitate separated in 10 or 15 minutes, and the filtrate was
o contain only 0.2 to 0.4 mg. Tl.—A mixture containing 1 mg. Tl as TlCl, 2
Fe as $FeCl_3$, 200 mg. Mn as $MnCl_2$ and 200 mg. Al as $AlCl_3$ was treated by P.
iltrate was evaporated nearly to dryness and tested for thallium by *P. 65*d*:
ipitate of TlI separated.

P. 52, N. 8: Necessity of Adding Na_2CO_3 to Precipitate Barium.—1 and 2
s $BaCl_2$ were treated by P. 52, the final volume being about 30 cc.: on boiling
ipitate which was proved to contain barium appeared in both experiments,
was very slight in that with 1 mg.—These experiments were repeated, exce
o Na_2CO_3 was added: no precipitate appeared on boiling.

2 mg. Cr and 100 mg. Ba as chlorides were treated by P. 52, except that no
was added: the filtrate was colorless, and the solution obtained on dissolving t
ipitate in HNO_3 was yellow, showing that the chromium had been precipit
$BaCrO_4$. —The experiment was repeated with 1 mg. Cr and 100 mg. Ba, exce
Na_2CO_3 was added: the filtrate was yellow, showing that the addition of Na_2CO_3
hromium to pass into the filtrate even when a large amount of barium is p

Solubility of Zinc Carbonate in NaOH.—50 mg. Zn as nitrate were dissolve
c. water and an equivalent amount of Na_2CO_3 added: a white precipitate sep
; cc. more 10 per cent. NaOH solution were added· the precipitate dissolved.
nore NaOH and 10 cc. 10 per cent. Na_2CO_3 solution were added, and the
eated to boiling: no precipitate separated. More Na_2CO_3 was added: a pre
inally formed.

P. 52, N. 9: Solubility of the Phosphates of Aluminum and Zinc in NaO
ng. Zn and 100 mg. Al as phosphates were dissolved in separate experiment
c. water and a very little HNO_3 (1.20); 10 per cent. NaOH was added slowl
ipitates separated but dissolved when an excess of about 4 cc. had been added

Partial Decomposition of Phosphates on Treating with Sodium Hydroxide.—
Mg, 50 mg. Ca, and 20 mg. (ferric) Fe, all as freshly precipitated phosphates were
eparately with about 30 cc. 4 per cent. NaOH solution for 3 or 4 minutes in
asseroles; the mixtures were filtered, the precipitates being washed with dilute
he filtrates were made strongly acid with HNO_3, and the precipitates were di
n HNO_3. Each solution was evaporated to a small volume and treated with
c. ammonium molybdate solution. The amount of phosphate in each soluti
stimated by the amount of yellow precipitate that had separated out after

hours: in the case of magnesium only a very small proportion of the phosphate remained in the precipitate; in the case of the iron about one-fifth remained in the precipitate; and in the case of calcium the phosphate was about equally divided between precipitate and filtrate.

Behavior of Calcium Borate and Oxalate towards Sodium Hydroxide.—A mixture containing 100 mg. Ca as $CaCl_2$ and 80 mg. BO_3 as H_3BO_3 was treated by P. 52; the precipitate was tested for borate by adding to it in a casserole H_2SO_4 (1.84) and alcohol, igniting the alcohol and stirring vigorously: no green color appeared. The filtrate was acidified with H_2SO_4, evaporated, and tested in the same way: a large amount of borate was found. A trial experiment showed that 5 mg. BO_3 could easily be detected in this way.

A mixture containing 500 mg. Fe as $FeCl_3$, 500 mg. C_2O_4 as oxalic acid, and 100 mg. Ca as $CaCl_2$ was treated by P. 52; the filtrate was analyzed for oxalate by acidifying, adding NH_4OH and $CaCl_2$: a very large precipitate of calcium oxalate separated. —The experiment was repeated with 300 mg. Ca and 500 mg. C_2O_4 (but no iron): the result was the same. The precipitate was tested for oxalate by dissolving it in HCl and adding NH_4OH: a small precipitate separated, showing that a large proportion of the oxalate had passed into the filtrate.

Decomposition of Oxalic Acid by Acids.—10 and 100 mg. oxalic acid were treated separately by P. 61, about 1 g. $KClO_3$ being added to the concentrated HNO_3 solution. The solutions were finally evaporated to almost 5 cc., diluted to 30 cc., neutralized with NH_4OH, and tested for oxalate by adding 10 cc. of 10 per cent. $Ca(NO_3)_2$ solution: no precipitate separated in either experiment.—The experiment with 10 mg. oxalic acid was repeated, except that no $KClO_3$ was added to the HNO_3 solution: a precipitate containing about 3 mg. oxalic acid resulted.—10 mg. oxalic acid were added to 15 cc. HCl (1.20), the mixture was evaporated to 2 or 3 cc., diluted and tested for oxalic acid as above: a precipitate of calcium oxalate separated that was estimated to correspond to 3 or 4 mg. oxalic acid.—The experiment was repeated with aqua regia instead of HCl (1.20): somewhat more oxalic acid was decomposed, but at least 2 mg. remained.—These experiments prove that the decomposition of oxalic acid is very rapid in a hot mixture of HNO_3 and $HClO_3$, much slower in aqua regia, and still slower in HCl (1.20) or HNO_3 (1.42).

P. 52, N. 10: Color of an Alkaline Solution of Sodium Chromate and Peruranate.—1 mg. Cr as $KCrSO_4$ was treated by P. 52, the final volume being about 30 cc.: the yellow color of the solution was easily seen.

1 mg. U as $UO_2(NO_3)_2$ was treated by P. 52, the final volume being about 15 cc.: the solution was distinctly yellow.—The experiment was repeated with 5 mg. U; the solution had a reddish tinge. It was diluted to 30 cc.: the reddish color changed to yellow.

Color of Vanadium Solutions.—100 mg. V as Na_3VO_4 were added to a little concentrated HCl, and the mixture was evaporated to a small volume: the solution was at first orange-yellow but turned greenish blue on evaporation with HCl, showing reduction of the vanadium to the quadrivalent state. Excess of concentrated HNO_3 was added and the mixture again evaporated to a small volume: the solution rapidly became yellow and the concentrated solution was deep red, doubtless owing to the presence of free vanadic acid (See below). On diluting to about 20 cc., it became yellow. The solution was neutralized with 10 per cent. NaOH solution: a small yellow precipitate separated during the neutralization but dissolved on the addition of a little more NaOH; the alkaline solution was of a deeper yellow color than the dilute HNO_3 solution. Na_2O_2 was added: no change was observed. The mixture was boiled for 1 minute: the solution became colorless. The solution was cooled and made acid

with HNO_3: it became yellow, the color being deepest at the neutral point. To a portion of this acid solution were added 50 mg. Ti as $TiCl_4$: no change in color was observed, showing that the Na_2O_2 had been completely decomposed and that no pervanadate had remained in the alkaline solution after boiling. Düllberg, *Z. physik. Chem.*, **45**, 172 (1903), considers that the yellow color is due to $H_4V_6O_{17}^{\equiv}$, an ion of the tetrabasic hexavanadic acid, $H_4V_6O_{17}$ (see C. E., *P. 58*a*, N. 6).

P. 52, N. 11: Division of Zinc in the Sodium Peroxide Treatment.—500 mg. Fe as $FeSO_4$ and 10 mg. Zn as $ZnCl_2$ were treated by P. 52, the final volume being about 30 cc.; the filtrate was tested for zinc by P. 53 and 57: only about 3 mg. Zn were found, showing that the remainder had been carried down with the $Fe(OH)_3$.—The experiment was repeated with 5 mg. Zn as $ZnCl_2$: only a trace of zinc was found in the filtrate.—The last experiment (with 5 mg. Zn) was repeated except that a large excess of NaOH was added before the Na_2O_2: 1 to 2 mg. Zn were found in the filtrate. The precipitate of $Fe(OH)_3$ was analyzed by P. 64, 66 and 67: the remainder of the zinc was found.

500 mg. Mn as $MnCl_2$ and 10 mg. Zn as $ZnCl_2$ were treated by P. 52, and the filtrate was tested for zinc by P. 53 and 57: no zinc was found.—The experiment was repeated with 20 mg. Zn: a very small precipitate of ZnS was obtained in P. 57 which contained less than 0.5 mg. Zn. On analyzing the precipitate by P. 61, 64, 66 and 67 the zinc was found. Therefore nearly 20 mg. zinc may be completely carried down when 500 mg. Mn are present.—The experiment was repeated with 10 mg. Zn, except that the acid solution was poured into a fairly concentrated NaOH solution in P. 52: about 0.3 mg. Zn was found in the filtrate, showing that a little zinc remains in the filtrate in this case.

For the fact that zinc is carried down with nickel and cobalt, see T. A., No. 140–143.

Separation of Vanadium from Manganese.—A mixture containing 250 mg. Mn as nitrate and 1 mg. V as Na_3VO_4 was treated by P. 52; the filtrate was tested for vanadium by *P. 58*e*: a very good test was obtained.

P. 53, N. 1: Solubility of Zinc Phosphate, Carbonate, and Oxalate in Ammonium Hydroxide.—100 mg. Zn as $ZnSO_4$ along with an equivalent amount of sodium phosphate, sodium carbonate or oxalic acid were dissolved in separate experiments in about 30 cc. cold water and about 2 cc. HNO_3 (1.20). The solutions were neutralized with NH_4OH (0.96) and an excess of about 3 cc. added: clear solutions were obtained in each case.

P. 54, N. 1–3: Confirmatory Test for Aluminum.—See Knoevenagel, *Praktikum des anorg. Chemikers*, p. 160.

0.5 mg. Al and 0.2 mg. Co as nitrates were treated by P. 54: the ash retained the form in which the filter paper was rolled and had a brilliant blue color.—The experiment was repeated with 0.2 mg. Al and 0.1 mg. Co: the residue was distinctly blue.—The experiment was repeated with 0.1 mg. Al and 0.1 mg. Co: no blue color was apparent.

Effect of Other Elements upon the Confirmatory Test for Aluminum.—0.5 mg. Al and 0.2 mg. Co as nitrates were treated by P. 54, except that 1 mg. Fe as $Fe(NO_3)_3$ was also added: the residue was brown.—This experiment was repeated with 1 mg. Al: the residue was partly blue.—The experiment was repeated with 2 mg. Fe and 1 mg. Al: the blue color could scarcely be distinguished.

The experiment with 0.5 Al was repeated in the presence of 1 mg. Be as $Be(NO_3)_2$: the residue was blue.—The experiment was repeated with 5 mg. Be: a satisfactory test for aluminum was obtained.—The experiment with 1 mg. Al was repeated in the presence of 5 mg. Be and also of 10 mg. Be as nitrate: a fair test for aluminum was obtained in the presence of 5 mg. Be but none with 10 mg. Be. In the latter case the paper and ash disintegrated.

1 mg. Al as nitrate was treated by P. 54, in the presence of 1, 2, and 5 mg. U as $UO_2(NO_3)_2$ respectively: a slight test for aluminum was obtained in the first experiment, a very poor one in the second, and none in the third.—The experiment was repeated with 0.5 Al and 1 mg. U: the test was very poor.

The experiment was repeated with 1 mg. Al and 5 mg. V as Na_3VO_4: the residue was distinctly blue.

0.5 mg. Al as $Al_2(PO_4)_3$ and 0.2 mg. Co as nitrate were treated by P. 54: the residue was blue.

1 mg. Al as nitrate was precipitated by adding to it $NaHCO_3$ solution and boiling. The precipitate was filtered off, washed once and treated by P. 54: the ash fused together into a small mass and no blue color was apparent.—1 mg. Al and about 5 mg. Na as nitrates were then treated by P 54: the result was the same, showing that the failure in the first experiment had been due to the presence of a sodium salt.

50 mg. SiO_2 as Na_2SiO_3 were dissolved in about 2 cc. HNO_3 (1.20) and 30 cc. water, heated to boiling, and made alkaline with NH_4OH: the solution slowly became turbid, and a gelatinous precipitate separated. This was collected on a filter, washed, and a portion of hot HNO_3 (1.20) was poured through the filter two or three times: the silica did not dissolve. The HNO_3 solution was tested for aluminum by P. 54, 0.5 mg. Co as nitrate being added: the residue was black.—The experiment was repeated except that 2 mg. Al as nitrate were also present: a fair test for aluminum was obtained.

P. 56, N. 1: Test for Chromate with Hydrogen Peroxide.—For the constitution and properties of the perchromic acid, and of other perchromates, see Riesenfeld, *Ber.*, 38, 1885, 3380, 4578, and 4068 (1905).

In a series of test tubes, each of which contained 0.3 mg. Cr as K_2CrO_4, were placed 0, 0.5, 2, 5, 10, and 20 cc. HNO_3 (1.20); each solution was diluted to 20 cc.; 3–5 cc ether and 2 cc. H_2O_2 (3 per cent.) were added, and the solutions were shaken: in the solution containing no acid, and in the solutions containing 5, 10, and 20 cc. acid, no blue color was obtained, but the remaining two solutions became blue at once, and the blue compound was extracted by the ether on shaking. In the solution containing 2 cc. HNO_3, the color in the ether layer in contact with the solution disappeared in about half an hour on standing; the color was more brilliant and remained for a longer time in the experiment with 0.5 cc. HNO_3.—The experiment was repeated with H_2SO_4 (1.20) instead of HNO_3: no color was obtained with no acid or with 10 and 20 cc. of it; the most brilliant and most permanent color was obtained in the experiment with 0.5 cc. acid.—The experiment was repeated with 30 per cent. acetic acid: in this case the best tests were obtained in the solutions containing 10 and 20 cc. of acid; with the more delicate solutions only a faint blue color was obtained.

Another series of experiments was performed with solutions that contained 0.3 mg. Cr as K_2CrO_4, and 2 cc. HNO_3 (1.20) in about 20 cc.; 3 cc. ether and varying amounts of H_2O_2 (3 per cent.) were added: with 10 cc. H_2O_2 no test was obtained, with 5 cc. a slight one, with 2 cc. a good test, but with 0.5 cc. H_2O_2 a much better one.

In all of these experiments in which the blue perchromic acid was formed, the blue color disappeared completely in less than 1 hour. In some of them the solution was warmed to 50 or 60°: the blue color disappeared very rapidly. These experiments prove that perchromic acid is a very unstable substance even in the absence of an excess of H^+ or of H_2O_2 and is still more so at higher temperatures.

Delicacy of the Confirmatory Test for Chromate.—To a solution containing 0.5 cc. Cr as K_2CrO_4 in 100 cc. was added a little ammonium acetate solution, 2 cc. acetic acid, and 1 g. $BaCl_2$: a yellow precipitate separated at once. This was collected on

a filter, and treated by P. 56: upon the addition of H_2O_2 and ether, a distinc color resulted. The experiment was repeated with 0.2 mg. Cr: a slight but d precipitate and color were obtained.

Reduction of Chromic Acid by Filter Paper.—10 mg. Cr as K_2CrO_4 were precip as lead chromate, and the mixture filtered. The precipitate, with the filter, was in a casserole; 10 cc. water, and 5 cc. HNO_3 (1.20) were added, and the mixtu boiled. The solution turned green in about 1 minute, thus showing that red takes place readily.

P. 57, N. 3: Ignition Test for Zinc with Cobalt Nitrate.—0.1, 0.2 and 10 mg. $Zn(NO_3)_2$ were treated as described in the second paragraph of P. 57, 0.2 mg. nitrate being used in each experiment: a distinct green color resulted in the ment with 0.1 mg. Zn, a deeper color with 0.2 mg. and an intense color with —1 mg. Zn and 2 mg. Co as nitrates were treated as described in the last par of P. 57: the residue was green. The residue was then heated strongly: it black, showing that when an excess of cobalt is present the test is more delicate mixture is not heated strongly.—The experiment was repeated with 2 mg. Cr mg. Zn: a green color resulted which remained after the residue had been strongly.

A solution containing 5 mg. Zn and 0.5 mg. Co as nitrates was evaporated t ness in a casserole and the mixture was ignited, first gently and then strong residue was black owing to the presence of cobalt oxide.—0.3 mg. Zn and o Co as nitrates were treated by the last paragraph of P. 57, except that 5 cc. of cent. Na_2CO_3 solution were added in excess: only a very faint green color re —The experiment was repeated except that only 3 drops Na_2CO_3 solution were in excess: the green color was mixed with black.—The experiment was repeate an excess of 1 cc. and also with an excess of 0.5 cc. Na_2CO_3 solution: a good gree was obtained.—These experiments show that some Na_2CO_3 must be added, bu a moderate quantity.

A solution containing 0.3 mg. Zn and 0.2 mg. Co as chlorides and an exce was treated by P. 57 (last par.), no HNO_3 being added: the residue had no c color, showing that HCl cannot be substituted for HNO_3.

P. 58a, N. 3: Composition of the Zinc and Beryllium Precipitates Produced dium Hydrogen Carbonate.*—500 mg. Zn as nitrate were treated by *P. 58a, a total volume of 100 cc. The precipitate was carefully washed with water, and for carbonate in the usual way by treating with acid in a flask and passing t evolved through $Ba(OH)_2$ solution. A large precipitate of $BaCO_3$ was obtained corresponded to at least 200 to 300 mg. Zn.—The experiment was repeated wi mg. Be: a large amount of carbonate was also found in the beryllium precipita precipitate of $BaCO_3$ being about twice as large as in the experiment with zinc. sons states, *J. Am. Chem Soc.*, **28, 557 (1906), that the precipitate obtained in a ammonium carbonate solution is a basic carbonate of beryllium.

Precipitation of Aluminum in Hot Sodium Hydrogen Carbonate Solutions in a Bottle.—Solutions containing 2 mg. Al as nitrate in 100 cc. were placed in p bottles, and 2, 5 and 10 mg. $NaHCO_3$ added: each of the three solutions quickly turbid in the cold. The bottles were heated at about 95° in a water bath f an hour: a flocculent precipitate formed in each case in less than 5 minutes, a tled in less than 20 minutes. The bottles were cooled and the precipitates off; the filtrates were evaporated with excess of HNO_3 and tested for aluminu NH_4OH: little or no precipitate separated, showing that the precipitation of th minum had been practically complete in each case.—The experiments were re with 1, 1/4, 1/16, and 1/32 g. $NaHCO_3$: the results were the same except th

precipitation was not complete with 1/32 g. $NaHCO_3$.—The experiment was repeated with 1/64 g. $NaHCO_3$: no precipitate was obtained.—These experiments were repeated, except that the solution was thoroughly saturated with CO_2 gas before adding the $NaHCO_3$: the results were nearly the same.

A solution containing 500 mg. Al as nitrate in 100 cc. was placed in a bottle and 4 g. $NaHCO_3$ added: there was a violent evolution of CO_2 gas, a small precipitate formed, and the solution still reacted acid to litmus. One g. more $NaHCO_3$ was added: a very large precipitate separated, very little gas came off, and the solution after shaking did not turn blue litmus red. The mixture was heated in the closed bottle at 95° in a waterbath for half an hour, cooled, and filtered: the filtrate was found to contain no aluminum. Therefore 500 mg. Al are completely precipitated when about 5 g. $NaHCO_3$ are added in 100 cc. of solution.

Precipitation of Zinc Carbonate in Hot Sodium Hydrogen Carbonate Solutions.—Four solutions, each containing 2 mg. Zn as nitrate dissolved in 100 cc., were poured into strong 200 cc. bottles; to these were added 1, 2, 3 and 5 g. respectively of solid $NaHCO_3$; the bottles were corked and shaken until the $NaHCO_3$ dissolved; they were then heated in a waterbath at 90 to 95° for half an hour: all the solutions became slightly turbid in the cold and after heating for 5 minutes precipitates could be seen in suspension. After the half hour's heating the bottles were allowed to cool to about 40°, and the solutions containing 1 and 5 g. $NaHCO_3$ were filtered and tested for zinc by evaporating with HNO_3, adding NH_4OH and acetic acid and passing in H_2S: only a trace of zinc was found in each filtrate, thus showing that the precipitation was practically complete in both 1 per cent. and 5 per cent. $NaHCO_3$ solutions.—The experiments with 1 and 2 g. $NaHCO_3$ were repeated except that the solutions were thoroughly saturated with CO_2 gas at room temperature before the $NaHCO_3$ portions were added: the results were the same.

The experiment was repeated with a solution containing 500 mg. Zn as nitrate in 100 cc., 2 g. $NaHCO_3$ being added: no precipitate of ZnS separated. The experiment was repeated with 500 mg. Zn and 1.5 g. $NaHCO_3$: about 5 mg. Zn were found in the filtrate, showing that 1.5 g. $NaHCO_3$ is not quite sufficient to precipitate 500 mg. Zn completely.

Precipitation of Beryllium in Hot Sodium Hydrogen Carbonate Solutions in a Closed Bottle.—A solution containing 1 mg. Be as nitrate in 100 cc. was placed in a 200 cc. bottle, 1 g. $NaHCO_3$ was added, and the mixture was digested in the tightly stoppered bottle at about 95° in a waterbath for half an hour: the solution became turbid in less than 5 minutes and a precipitate separated in 10 minutes; on standing in the cold for an hour the precipitate seemed to redissolve to a small extent. The experiment was repeated with a solution that was saturated with CO_2 gas before the $NaHCO_3$ was added: the result was the same.—These experiments were repeated with 1 mg. Be and 2 g. $NaHCO_3$: the mixture that had been saturated with CO_2 was distinctly turbid in 15 minutes while the other was only very slightly turbid after half an hour. The solutions cleared on standing for an hour in the cold.—The last experiments were repeated with 2 mg. Be and 2 g. $NaHCO_3$: distinct precipitates were obtained corresponding to about 1 mg. Be but these redissolved to a considerable extent in the cold.

These experiments were repeated with solutions containing 3 to 10 g. $NaHCO_3$ in 100 cc. of solution and varying quantities of beryllium: in the 3 per cent. $NaHCO_3$ solution 3 mg. Be gave no precipitate, but a larger amount did so; in the 5 per cent. solution, about 15 mg. Be just remained in solution in 100 cc.; and in the 10 per cent. solution, about 75 mg. Be gave a small precipitate in 50 cc., while 50 mg. Be gave only a negligible precipitate.

Solubility of Uranyl Vanadate in Sodium Hydrogen Carbonate Solutions.—Solutions

containing 100 mg. U as $UO_2(NO_3)_2$ and 60 mg. V as Na_3VO_4 were mixed, a few drops HNO_3 (1.20) were added to dissolve the precipitate, the mixture was diluted to 100 cc., 2 g. $NaHCO_3$ were added, and the mixture was digested in a closed bottle at 95° for half an hour: no precipitate separated. The mixture was cooled down, 40 mg. V as Na_3VO_4 were added, making 100 mg. in all, and the mixture was again heated at 95° for half an hour: no precipitate separated in the hot solution, nor in the cold on standing several days.—The experiment was repeated with 100 mg. U and 100 mg. V, except that the mixture was first treated with NaOH and H_2O_2 by P. 52, and that 1.5 g. $NaHCO_3$ were used instead of 2 g.: the result was nearly the same.—100 mg. U as $UO_2(NO_3)_2$, 100 mg. V as Na_3VO_4, and 3 g. $NaNO_3$ were treated by *P. 58*a*, 1 g. excess of $NaHCO_3$ being added: a precipitate formed on adding $NaHCO_3$ and a considerable one remained after heating the mixture at 100° in a closed bottle for 30 minutes. The precipitate and filtrate were analyzed for uranium and vanadium by *P. 58*c–e*: the filtrate was found to contain 35–40 mg. of uranium and all but 10 or 15 mg. of the vanadium.

The last experiment was repeated except that the mixture was warmed in a flask at 95° (without allowing it to boil) for 30 minutes: the precipitate that remained was smaller, and contained only 10 to 20 mg. U and 2 to 5 mg. V.—The last experiment was repeated except that the mixture was boiled for 1 minute in an open flask: the precipitate dissolved completely, and no precipitate formed on cooling even in 24 hours, showing that uranyl vanadate is more soluble in slightly alkaline carbonate solutions than in those from which the CO_2 is prevented from escaping.

An acid solution containing 50 mg. V as Na_3VO_4, and 50 mg. U as $UO_2(NO_3)_2$ was diluted to 100 cc. and neutralized by adding a little powdered $NaHCO_3$. Then 0.5 g. $NaHCO_3$ was added, and the mixture was heated in a pressure bottle at 95° for half an hour: on heating a large precipitate remained.—To a solution containing 100 mg. V as Na_3VO_4, 20 mg. U as $UO_2(NO_3)_2$ and a known excess of HNO_3 (1.20) in 50 cc. (instead of 100 cc.) was added just sufficient $NaHCO_3$ to leave 1 g. undecomposed $NaHCO_3$. The mixture was heated in a closed bottle at 95° for half an hour: no precipitate separated.—To this solution after cooling, was added 20 mg. more U and the mixture was again heated at 95°: a large precipitate separated in the cold and remained on heating.—The experiment was repeated with 100 mg. U and 10 mg. V: no precipitate separated. 10 mg. more V were added and the heating repeated: a large precipitate separated in the cold and remained on heating.—The last experiment was repeated with 100 mg. V and 100 mg. U and the precipitate and filtrate were analyzed for uranium and vanadium by *P. 58*c* to *e*: the filtrate was found to contain 20 or 30 mg. of uranium and all but a few mg. of the vanadium.

Non-Precipitation of Uranyl Chromate, Phosphate, and Oxalate in the $NaHCO_3$ Procedure.—To a solution containing 100 mg. U as $UO_2(NO_3)_2$ 200 mg. Cr as K_2CrO_4, and a known (small) amount of HNO_3 (1.20) in 100 cc. was added enough $NaHCO_3$ to leave 1 g. of the undecomposed carbonate; the mixture was heated in a closed bottle at 95° for half an hour: no precipitate separated.—A solution containing 100 mg. U as $UO_2(NO_3)_2$ and 100 mg. PO_4 as $NaHPO_4$ was treated by P. 52 and then by *P. 58*a*: no precipitate separated in the $NaHCO_3$ procedure. After cooling an additional 250 mg. portion of PO_4 was added, and the heating repeated: no precipitate separated.—The experiment was repeated with 100 mg. V as Na_3VO_4 and 200 mg. oxalic acid: no precipitate separated.

**P. 58*a*, N. 4: Precipitation of Aluminum, Zinc, and Beryllium in Hot Sodium Hydrogen Carbonate Solutions in Open Flasks.*—2 mg. Al as nitrate and 3 g. $NaNO_3$ were dissolved in 100 cc. water; a little $NaHCO_3$ was added until the mixture after shaking just ceased to react acid to litmus paper; 1 g. more was added; the mixture was heated to about 90° and digested at this temperature in a covered flask on a waterbath for

half an hour: the precipitate slowly dissolved, except a few small flakes. The mixture was filtered while hot, and the filtrate tested for aluminum by acidifying with acetic acid, adding Na_2HPO_4 and heating to boiling: almost all the aluminum was found in the filtrate.—This experiment was repeated twice with 2 mg. and with 1 mg: the results were the same.—The experiment was repeated twice with 20 mg. Al: the filtrate contained less than 1 mg. Al.

The experiments with 2 and 20 mg. were repeated, except that CO_2 gas was passed through the mixture: the results were nearly the same, except that the filtrate may have contained somewhat more aluminum, showing that there is no advantage in using CO_2 gas.

The experiment with 20 mg. Al was repeated except that the mixture was boiled for one minute: the filtrate contained 3 or 4 mg. Al.—The experiment was repeated except that the mixture was allowed to cool before filtering: the filtrate contained about 1 mg. Al.—The experiment was repeated with 4 mg. Al: the precipitate disappeared completely on boiling, but a precipitate separated out on cooling.—The experiment was repeated with 6 mg. Al: a very small precipitate remained on boiling 1 minute.

1 mg. Zn as nitrate and 2 g. $NaNO_3$ were dissolved in 100 cc., 1 g. excess $NaHCO_3$ was added, and the mixture boiled in a flask for one minute: the precipitate did not dissolve and was proved to contain zinc by P. 53–57.—The experiment was repeated with 20 mg. Zn; the filtrate being tested for zinc by acidifying with HNO_3, boiling, adding NH_4OH and passing in H_2S: no precipitate formed, showing that the zinc was completely precipitated.

10 mg. Be as chloride and 2 g. $NaNO_3$ were dissolved in 100 cc. water, $NaHCO_3$ was added until the mixture after shaking just ceased to react acid to litmus paper; 1 g. more was added; the mixture was boiled for 1 minute, and filtered while hot; the filtrate was acidified with HNO_3, evaporated to about 15 cc. and tested for beryllium by adding NH_4OH: the filtrate contained only about 0.1 mg. Be.—The experiment was repeated except that the mixture was allowed to cool before filtering: the filtrate contained about 0.3 mg. Be.—The experiment was repeated with 1 mg. Be: the precipitate remained on boiling for one minute, and did not disappear on standing in the cold for several hours.

These experiments were repeated with solutions containing from 1.5 to 5 g. $NaHCO_3$ in 100 cc. of solution and varying quantities of beryllium: in a 1.5 per cent. $NaHCO_3$ with 1 mg. Be little or no precipitate remained on boiling 1 minute; in a 2 per cent. solution no precipitate remained with 2 mg. Be, but one remained with 4 mg.; in a 3 per cent. solution 40 mg. Be dissolved almost completely, but 50 mg. gave a large precipitate. A comparison of these results with those obtained in a similar series of experiments in closed bottles (C. E., N. 3, above) shows that considerably more beryllium dissolves in concentrated $NaHCO_3$ solutions when the CO_2 is allowed to escape.

**P. 58a, N. 5: Precipitation of Uranium with Aluminum or Beryllium in Hot Dilute Sodium Hydrogen Carbonate Solutions.*—See T. A., No. 171 to 175. In an analysis with 200 mg. Al and 10 mg. U, starting at *P. 58a, 1 or 2 mg. U were found in *P. 58c–d.

P. 58a, N. 6: Dissociation Relations of Carbonic Acid.*—See McCoy, *Am. Chem. J.*, **29, 437 (1903).

Dissociation Relations of Chromic Acid.—See Spitalsky, *Z. anorg. Chem.*, **54**, 265 (1907) and Sherrill, *J. Am. Chem. Soc.*, **29**, 1641 (1907). The work of the latter shows that H_2CrO_4 dissociates in steps, first into $HCrO_4^-$ and then into $CrO_4^=$, that the $HCrO_4^-$ is a very weak acid, and that the latter even in dilute solution is converted

by dehydration in large measure but by no means wholly, into dichromate-ion ($Cr_2O_7^{=}$).

Condition of Vanadic Acid in Solution.—See Düllberg, *Z. physik. Chem.*, **45**, 129–181 (1903). He considers that in a solution of the composition of Na_3VO_4, which reacts strongly alkaline, the salt is largely hydrolyzed according to the reaction $2Na_3VO_4 + H_2O = 2NaOH + Na_4V_2O_7$, but his evidence is not convincing. On adding HCl slowly the results indicate the presence of a tetrabasic acid, $H_4V_6O_{17}$. This is a strong acid, two of the hydrogens splitting off nearly completely in dilute solutions, and the third one to a considerable extent. The yellow color is probably due to the ion $HV_6O_{17}^{\equiv}$. The transition of one form of vanadic acid into another takes place readily, the final equilibrium state being reached fairly quickly. Conductivity and freezing-point determinations make it probable that the formula of sodium metavanadate is $(Na^+)_3V_3O_9^{\equiv}$.

**P. 58b, N. 1: Partial Decomposition of H_2O_2 in the $NaHCO_3$ Treatment.*—A mixture containing 100 mg. U as $UO_2(NO_3)_2$ and 100 mg. V as Na_3VO_4 was treated by P. 52 and *P. 58*a* and then was acidified with HNO_3: the acid solution before adding the $NaHCO_3$ was red owing to the presence of pervanadic acid, indicating the presence of much H_2O_2; on neutralizing with $NaHCO_3$ it became yellow; and the final HNO_3 solution was also pale yellow. The solution was tested for H_2O_2 with a titanium solution: a distinct color was obtained. These results show that much but not all of the H_2O_2 had been decomposed.

**P. 58b, N. 2: Detection of Chromic Acid in the Presence of Uranium and Vanadium by H_2O_2.*—A mixture containing 1 mg. Cr, 100 mg. U, 100 mg. Zn and 100 mg. Al as nitrates, and 100 mg. V as Na_3VO_4 was treated with NaOH and Na_2O_2 by P. 52: a deep red solution resulted and there was no residue. The solution was made acid with HNO_3, being cooled carefully during the process. Just enough acid was added to dissolve the precipitate that formed. To about one-fourth of the solution in a test-tube was added a little ether and about 1 cc. H_2O_2: the ether layer became blue. The water layer was red before H_2O_2 was added, showing the presence of pervanadic acid. —The experiment was repeated with 2 mg. Cr, 100 mg. U and 100 mg. V: the result was the same. After testing for chromium the remainder of the solution was treated by *P. 58*a*, the solution was cooled, made just acid with HNO_3, and one-tenth of it tested for chromic acid with H_2O_2: a good blue color was obtained. The remainder of the solution was made somewhat more strongly acid and evaporated to half its volume; the test for chromic acid was then made with half the solution: no blue color was obtained, showing that the chromic acid had been reduced on boiling.

Action of H_2O_2 on Uranium Salts.—To 10 mg. U as $UO_2(NO_3)_2$ in 20 cc. were added 1 cc. HNO_3 (1.20), 1 cc. 3 per cent. H_2O_2, and a little ether: the yellow color of the solution did not change, and the ether layer remained colorless.

**P. 58b, N. 4: Precipitation of Chromate by Lead Nitrate.*—Several solutions each containing 0.5 mg. Cr as K_2CrO_4, 2 g. $NaNO_3$, and 1 g. $NaHCO_3$ in 100 cc. or 70 cc. were made distinctly acid with HNO_3, shaken to expel CO_2, and neutralized exactly with NaOH; varying amounts of HNO_3 (1.20) were added, and finally known volumes of a 20 per cent. lead nitrate solution. The results are shown in the following table:

Initial volume.	Volume of HNO_3 (1.20).	Volume of lead nitrate solution.	
100 cc.	1.5 cc.	10 cc.	precipitate in 1 or 2 min.
100 cc.	2.5 cc.	20 cc.	precipitate in 3 or 4 min.
100 cc.	5.0 cc.	30 cc.	no precipitate in 30 min.
70 cc.	1.5 cc.	10 cc.	precipitate in 2 or 3 min.
70 cc.	2.5 cc.	10 cc.	precipitate very slowly.
70 cc.	2.5 cc	20 cc.	precipitate in 3 to 5 min.

The last two experiments were repeated with 6 g. $NaNO_3$ (instead of 2 g.): only very small precipitates were obtained in half an hour, even with 20 cc. $Pb(NO_3)_2$ solution, showing that the presence of much $NaNO_3$ prevents the precipitation of $PbCrO_4$.

Behavior of Vanadate and Uranate towards Lead Nitrate.—Several solutions, each containing 100 mg. V as Na_3VO_4, 2 g. $NaNO_3$ and 1 g. $NaHCO_3$, in 100 cc., were acidified with HNO_3, shaken, and then neutralized exactly with NaOH; 1.5 to 3 cc. of HNO_3 (1.20) and 10 to 30 cc. of a 20 per cent. lead nitrate solution were added and the mixture allowed to stand 30 minutes: with 3 cc. HNO_3 there was no precipitate even with 30 cc. $Pb(NO_3)_2$; with 1.5 and 2 cc. HNO_3 there was none with 10 cc. $Pb(NO_3)_2$; but a small one with 20 cc., which was however very slight when 2 cc. HNO_3 were used. The experiments were repeated with an initial volume of 70 cc.: the results were nearly the same, except that the precipitates when formed were somewhat larger.

A solution containing 100 mg. U as $UO_2(NO_3)_2$, 2 g. $NaNO_3$, and 1 g. $NaHCO_3$ in 100 cc. was neutralized with HNO_3, and an excess of 1 cc. HNO_3 (1.20) was added; finally 20 cc. 20 per cent. $Pb(NO_3)_2$ were added: no precipitate separated in several hours.

*Precipitation of Aluminum, Beryllium or Lead by Sodium Phosphate in *P. 58c.*—0.5, 1, and 2 mg. Al as nitrate, in solutions containing 2 g. $NaNO_3$, 2 g. NH_4NO_3, and 5 cc. 30 per cent. acetic acid in a total volume of 100 cc. were heated to boiling: flocculent white precipitates separated in each case, the results showing that this is a very good method of estimating small amounts of aluminum.

The experiments were repeated with 0.5, 1 and 2 mg. Be as chloride: flocculent white precipitates resulted except in the experiment with 0.5 mg. The filtrate in the experiment with 2 mg. was estimated to contain about 0.5 mg. Be.

The experiments were repeated with 1 and 2 mg. Pb as nitrate: a distinct precipitate was obtained with 2 mg. but only a very small one with 1 mg. Pb.

Oxidation of Hypovanadic Acid by Bromine.—50 mg. V as Na_3VO_4 and 1 g. Pb as $Pb(NO_3)_2$ were dissolved in 2.5 cc. HNO_3 (1.20) and 100 cc. water; the mixture was saturated with H_2S in the cold, filtered, and the filtrate was boiled: the cold solution had a blue color, but on boiling sulphur separated and the color became deeper. The sulphur was filtered off, bromine water added until the bromine odor was distinct after shaking, and the mixture was boiled: the color was still blue. A small excess of bromine was again added: the solution was still blue.—The experiment was repeated except that several drops liquid bromine were added, and the mixture shaken, and allowed to stand two or three minutes; the bromine was then boiled off: the solution was yellow. The filtrate was treated by *P. 58*c*: no precipitate separated.

Behavior of Vanadyl Salts and Vanadates towards Sodium Phosphate.—50 mg. V as Na_3VO_4 and 1 g. Pb as $Pb(NO_3)_2$ were dissolved in 2.5 cc. HNO_3 (1.20) and 100 cc. water; the mixture was saturated with H_2S, filtered, boiled and filtered again. The blue filtrate was treated by *P. 58*c*, 2 g. $(NH_4)_2SO_4$ and 2 g. Na_2HPO_4 being added: on warming, a large, flocculent, bluish white precipitate separated.—The experiment was repeated except that the vanadyl salt was first oxidized with liquid bromine as described in P. 58*b*: no precipitate separated in *P. 58*c*.

P. 58c, N. 1: Precipitation of Uranyl Ammonium Phosphate.*—See Kern, *J. Chem. Soc.*, **23, 705–10 (1901).

Detection of Small Amounts of Uranium.—0.3, 0.5 and 1 mg. U as $UO_2(NO_3)_2$ were dissolved in separate experiments in 100 cc. water containing 5 cc. 30 per cent. acetic acid and 3 g. $NaNO_3$, and treated by P. 58*c*: white flocculent precipitates separated in each case, but that with 0.3 mg. was very small. The precipitates were filtered off and tested by P. 58*d*: in the experiment with 0.3 mg. U the ferrocyanide test failed, but was very satisfactory in the other two cases.—The experiment with 0.3 mg. U

was repeated except that 0.5, 4, and 6 g. respectively $(NH_4)_2SO_4$ (instead of 2 g.) were added: very small precipitates of uranyl ammonium phosphate were obtained in each case, but the ferrocyanide test failed. This shows that there is no advantage in adding more than 2 g. $(NH_4)_2SO_4$.—The experiments with 0.5 and 1 mg. U were repeated, except that no ammonium salt was added: with 1 mg. the result was satisfactory, but with 0.5 mg. the confirmatory failed.

The first experiments with 0.3, 0.5 and 1.0 mg. U were repeated in a volume of 40 cc. instead of 100 cc.: a distinct phosphate precipitate resulted in each case, and the ferrocyanide test was satisfactory, even with 0.3 mg. With 0.2 mg. a small phosphate precipitate formed but the confirmatory test failed.—The experiment was repeated with 1.0 mg. U, except that 0.3 g. $Na_2HPO_4.12H_2O$ was added instead of 2 g.: the confirmatory test failed, showing that a large excess of Na_2HPO_4 is necessary.—The experiment with 0.3 mg. U was repeated except that 10 cc. acetic acid was used instead of 5 cc.: the confirmatory test failed, showing that a large excess of acetic acid makes the phosphate precipitation less complete.

Separation of Uranium and Vanadium by Phosphate:—100 mg. U as $UO_2(NO_3)_2$, 50 mg. V as Na_3VO_4, and 1 g. NH_4NO_3 were dissolved in a few drops HNO_3 and 30 cc. water. The mixture was neutralized with NH_4OH: a large pale precipitate of uranyl ammonium vanadate separated. 10 cc. 30 per cent. acetic acid were added: the precipitate did not dissolve. 5 cc. 10 per cent. ammonium phosphate were added, the mixture was heated to boiling, allowed to stand for 15 minutes, and filtered. The filtrate was tested for vanadium by *P. 58*e*: a large quantity was found. The precipitate was washed with dilute NH_4NO_3 solution, dissolved in dilute hydrochloric acid, and the phosphate precipitation repeated: less than 1 mg. V was now found in the filtrate. The phosphate precipitate was treated in the same way: less than 0.2 mg. V was found in it.—The complete experiment was repeated except that the mixture containing the uranium ammonium vanadate precipitate and the acetic acid was heated to boiling, cooled, and allowed to stand over night before the phosphate was added: the result was the same, showing that the vanadium passes into the filtrate even when it is first precipitated in combination with the uranium.

P. 58c, N. 4: Precipitation of Uranyl Hydrogen Phosphate.*—See Kern, *J. Am. Chem. Soc.*, **23, 705 (1901).

**P. 58d, N. 1: Behavior of Uranyl Salts towards Potassium Ferrocyanide.*—Known amounts of $K_4Fe(CN)_6$ solutions were added to solutions containing 0.5 mg. U as $UO_2(NO_3)_2$, 1 cc. HCl (1.12), and 10 cc. nearly saturated NaCl solution: with 4 cc. of a 3 per cent. ferrocyanide solution a brown color appeared only after 40 minutes, with 10 cc., a brown precipitate separated in about 10 minutes, while with 10 cc. of a 10 per cent. ferrocyanide solution a precipitate separated in a minute or two, showing that a large excess of $K_4Fe(CN)_6$ is needed to make the test delicate.—The experiment was repeated except that 0.5 cc. HCl (1.12) was added, instead of 1 cc., 10 cc. 3 per cent. ferrocyanide solution being added: a brown precipitate separated in a minute or two.—This experiment was repeated with 0.1 and 0.05 cc. HCl (1.12): brown precipitates separated at once.—The experiment was repeated without the addition of any acid: no brown color appeared.—The experiment was repeated, adding 5 cc. HCl (1.12): no brown precipitate separated in 1 hour, but the solution became blue and a blue precipitate separated slowly on account of the decomposition of the ferrocyanide.—These experiments show that a little acid must be present, but that much acid makes the test less delicate.

0.1 and 0.2 mg. U as $UO_2(NO_3)_2$ were treated by *P. 58*d*, a few mg. PO_4 as Na_2HPO_4 being added: a good test was obtained with 0.2 mg., but only a very poor one after

several minutes with 0.1 mg., showing that 0.1 mg. is about the limit of detectability, and that phosphate does not interfere with the detection of 0.2 mg. U.

The experiment with 0.5 mg. U and 0.5 cc. HCl (1.12) was repeated, except that water was added instead of NaCl solution: a dark red color resulted, and no precipitate separated out in 1 hour, showing that NaCl is needed to coagulate the colloid.

Behavior of Vanadyl Salts and Vanadic Acid towards Potassium Ferrocyanide.—5 mg. V as Na_3VO_4 after evaporation with HCl (whereby it is reduced to vanadyl chloride) were treated by *P. 58*d:* a greenish yellow precipitate separated. The precipitate was filtered off and the filtrate tested for vanadium by *P. 58*e:* only a very faint pink color resulted, showing that the precipitation of the vanadium by the ferrocyanide is nearly complete.—The experiment was repeated except that only two drops of HCl were added and the solution was not evaporated: no precipitate separated in half an hour, showing that a small quantity of vanadium in the form of vanadic acid is not precipitated by $K_4Fe(CN)_6$.

**P. 58e: Non-interference of Lead with the Vanadium Test.*—A solution containing 2 mg. Pb as $Pb(NO_3)_2$, and 0.5 mg. V as Na_3VO_4 and 2 g. NH_4NO_3 was treated by P. 58*e* and the black precipitate of PbS formed was filtered off: on saturating completely with H_2S, the filtrate had the characteristic violet-red color due to vanadium.

**P. 58g, N. 1: Separation of Aluminum and Beryllium.*—See Havens, *Z. anorg. Chem.*, 16, 15 (1898).

Precipitation of Aluminum as $AlCl_3.6H_2O$.—0.5 mg. Al as $AlCl_3$ was treated by *P. 58*g*, the total volume of the acid ether mixture being about 15 cc.: on saturating with HCl gas no precipitate could be seen, but on standing about 15 minutes a distinct crystalline precipitate separated out.

100 and 500 mg. Al as $AlCl_3$ were treated by *P. 58*g:* the filtrates, which had a total volume of about 70 cc., were evaporated to about 20 cc. and made alkaline with NH_4OH: no precipitate separated, but in the second experiment there was a faint turbidity corresponding perhaps to 0.1 mg. Al.

Behavior of Beryllium, Uranium and Chromium in the Hydrochloric Acid Ether Process.—100 mg. Be as $BeCl_2$ were treated by *P. 58*g*, the final volume being about 30 cc.: a small precipitate remained. This was filtered off, washed twice, dissolved in a little water, and proved to contain aluminum but no beryllium by boiling in a 10 per cent. $NaHCO_3$ solution as described in *P. 58*h*.

500 mg. Al and 2 mg. Be as chlorides were treated by *P. 58*g* in a volume of 60 cc. and the filtrate was treated by *P. 58*h:* a good test for beryllium was obtained and the amount of beryllium in the filtrate was estimated to be 1 or 2 mg., showing that very little beryllium was retained by the $AlCl_3.6H_2O$.

100 mg. U as UO_2Cl_2 were treated by *P. 58*g*, the total volume being 50 cc.: a clear yellow solution was obtained.

20 mg. Cr as K_2CrO_4 were boiled with HCl (1.20) to reduce the chromium to the chromic state, and the green solution was treated by *P. 58*g*, in a volume of about 30 cc.: the green color quickly disappeared and a violet precipitate separated. This was filtered off after several hours and the filtrate tested for chromium by evaporating, adding NH_4OH, and boiling: a precipitate estimated to contain 5–10 mg. Cr separated.

P. 58h, N. 1: Separation of Beryllium and Aluminum in Strong Sodium Hydrogen Carbonate Solution.*—See Parsons and Barnes, *J. Am. Chem. Soc.*, **28, 1589 (1906).

200 mg. Al as nitrate were dissolved in 20 cc. water, and added to a warm solution of 10 g. $NaHCO_3$ in 80 cc. water, the mixture was heated to boiling in a flask, boiled for 1 minute, and filtered; the filtrate was acidified with HNO_3, evaporated to about 20 cc. and made alkaline with NH_4OH: no precipitate separated on warming gently, nor on standing.

100 mg. Al and 1 mg. Be as nitrates were dissolved in 50 cc. water and 6 g. $NaHCO_3$ were added; the mixture was heated to boiling, boiled for 1 minute, and filtered while still hot; the filtrate was made acid with HNO_3, evaporated to about 10 cc. and made alkaline with NH_4OH: a very small precipitate separated which was estimated to contain 1/20 mg. Be.—The experiment was repeated with 2 mg. Be: the result was the same.—The experiment was repeated with 5 mg. Be: scarcely 1 mg. Be was found in the filtrate.—Therefore small amounts of beryllium cannot be completely separated from 100 mg. Al by this method.

The precipitate obtained in the experiment with 1 mg. Be was treated by *P. 58*g–h*: the beryllium present was estimated to be nearly 1 mg., showing that this separation with HCl and ether is more satisfactory than that with 10 to 12 per cent. $NaHCO_3$.

Behavior of Iron in Strong Sodium Hydrogen Carbonate Solution, and its Precipitation as Sulphide.—2 and 5 mg. Fe as $FeCl_3$ were treated by the last paragraph of *P. 58*h*: small precipitates of $Fe(OH)_3$ were formed in the $NaHCO_3$ solutions, but the precipitation was incomplete, for after acidifying the filtrates and adding NH_4OH, precipitates of $Fe(OH)_3$ were obtained, each of which was estimated to contain over 1 mg. Fe.—The experiment with 5 mg. Fe was repeated except that 5 cc. NaOH were added to the $NaHCO_3$ filtrate: no precipitate resulted in the cold, but about 0.5 mg. Fe as $Fe(OH)_3$ precipitated on boiling. The precipitation was still incomplete for about 0.5 mg. Fe was found in the solution on acidifying and adding NH_4OH.

0.5 mg. Fe as $FeSO_4$ and in a second experiment as $FeCl_3$, was boiled with 30 cc. 10 per cent. $NaHCO_3$, for 1 minute, the mixtures were poured through filters, cooled, and H_2S was passed in for about 3 seconds: the solutions became dark colored at once. After about 5 minutes the mixtures were filtered: the filtrates were clear, with a faint greenish shade corresponding to an insignificant amount of iron; more H_2S caused no further darkening.—The experiment with 0.5 mg. Fe as $FeCl_3$ was repeated, except that the $NaHCO_3$ solution was not cooled before passing in H_2S: a dark green solution was obtained which ran through the filter, showing that it is better to add the H_2S in the cold. To this solution (which was now cold) was added 2 or 3 mg. Fe as $FeSO_4$: on filtering after several minutes the filtrate was nearly colorless, and more H_2S gave no precipitate nor color.

**P. 58*h*, N. 2: Behavior of Uranyl Salts in Strong Sodium Hydrogen Carbonate Solution, and on Passing in H_2S.*—50 mg. U as UO_2Cl_2 (and in another experiment as $UO_2(NO_3)_2$) were dissolved in a little water and added to a solution containing 5 g. $NaHCO_3$, the final volume being 50 cc.; the mixture was boiled for 5 minutes: no precipitate separated.—The experiment was repeated with 5 mg. U as UO_2Cl_2 in a volume of 30 cc. and 10 cc. 10 per cent. NaOH was added to the 10 per cent. $NaHCO_3$ solution after boiling: no precipitate separated.

To a mixture containing 100 mg. Be and 20 mg. U dissolved in 50 cc. 10 per cent. $NaHCO_3$ was added 1 g. NH_4Cl, and the mixture was boiled: no precipitate separated.

A mixture containing 100 mg. Be and 10 mg. U (but no iron) dissolved in 30 cc. 10 per cent. $NaHCO_3$ solution was saturated completely with H_2S gas: no precipitate separated.

The Separation of Uranium and Beryllium by Potassium Ferrocyanide.—15 and 25 mg. Be as chlorides in HCl solution were evaporated almost to dryness, 10 cc. saturated NaCl solution added, the mixture was cooled and 5 cc. 10 per cent. $K_4Fe(CN)_6$ solution were added: clear solutions resulted which were blue colored, owing to the presence of a small amount of iron in the beryllium; after standing several hours a gelatinous light colored precipitate had separated in the experiment with 25 mg. Be.—The experiment was repeated with mixtures of 1 mg. U as $UO_2(NO_3)_2$ and with 5, 10, 15

and 20 mg. Be: a dark red color appeared at once in the experiments with 5 and 10 mg. Be, and on standing dark red precipitates settled out. In the experiments with 15 and 20 mg. the color was somewhat obscured owing to the presence of the iron. —The experiment with 20 mg. Be and 1 mg. U was repeated, except that the iron was first removed from the beryllium solution by P. 52: a good test for uranium was then obtained.

P. 61, N. 1: Solubility of Manganic Peroxide in HNO_3 in the Presence of Filter Paper. —500 mg. Mn as $Mn(NO_3)_2$ were treated by P. 52; the $MnO(OH)_2$ precipitate was boiled with 30 cc. HNO_3 (1.20) in a covered casserole for several minutes: very little of the precipitate dissolved. The experiment was repeated except that the filter, as well as the precipitate, was treated with the nitric acid: on boiling, the filter disintegrated and the precipitate dissolved completely in 10 or 15 min.—The last experiment was repeated with HNO_3 (1.42): nearly all of the precipitate dissolved after 5 minutes' boiling, and the remainder on standing over night. The solution obtained in the last experiment was evaporated to a small volume and diluted to about 15 cc.; the paper was filtered off, and the filtrate was treated by P. 61: the manganese was completely precipitated.

P. 62, N. 2: Precipitation of Manganese by Chloric and Nitric Acids.—See Hannay, *J. Chem. Soc.*, 23, 269 (1878); Ford, *Trans. Inst. Min. Eng.*, 9, 397.

P. 62, N. 3: Separation of Other Elements from Manganese by Chloric and Nitric Acids.—See T. A., No. 117, 118.

Iron.—100 mg. Mn as $MnCl_2$ and 1 mg. Fe as $FeSO_4$ were treated by P. 52 and P. 61 and the filtrate was tested for iron by P. 64: a good test was obtained.—500 mg. Mn as $MnCl_2$ and 1 mg. Fe were treated by P. 52 and then by P. 61; the precipitate and filtrate were tested for iron by evaporating with excess of HCl, diluting, and adding KSCN solution: a distinct test for iron was obtained in the filtrate but much more iron was found in the precipitate than in the filtrate.

Titanium.—A mixture containing 500 mg. Mn and 1 mg. Ti as nitrates was treated by P. 61; the filtrate was evaporated and made alkaline with NH_4OH: no precipitate separated, proving that the titanium had been completely carried down with the MnO_2.—This experiment was repeated with 5 and with 50 mg. Ti: the result was the same in each case.—The experiment was repeated with 50 mg. Mn and 50 mg. Ti; the precipitate was analyzed by *P. 62*a*, and about half the titanium found in it; the filtrate was evaporated almost to dryness: some of the titanium separated during the evaporation as a white precipitate which did not dissolve readily in HCl, but did in HF.—The experiment was repeated with 50 mg. Ti in the absence of manganese: no precipitate separated on adding $KClO_3$, nor on evaporating to 5 or 10 cc.

Zirconium.—A mixture containing 500 mg. Mn and 2 mg. Zr as nitrates was treated by P. 61; the filtrate was evaporated and made alkaline with NH_4OH: only a very small precipitate separated, showing that not quite all of the zirconium had been carried down.—The experiment was repeated with 50 mg. Zr: the filtrate was found to contain 15 or 20 mg. Zr. The manganese precipitate was treated by *P. 62*a*: the rest of the zirconium was recovered.

Vanadium.—A mixture containing 250 mg. Mn as nitrate and 1 mg. V as Na_3VO_4 was treated by P. 61: the filtrate was treated by *P. 58*e* to test for vanadium: no trace of vanadium was found. For the fact that vanadium is not carried down by manganese in the Na_2O_2 procedure see C. E., P. 52, N. 11.—The experiment was repeated with 250 mg. Mn and 10 mg. V: a mere trace of vanadium was found.—The experiment was repeated with 50 mg. Mn and 10 mg. V: not more than 1 or 2 V mg. were found in the filtrate.—The experiment was repeated with 20 mg. Mn and 10 mg. V: the filtrate contained not more than 2 or 3 mg. V.

Uranium.—A mixture of 250 mg. Mn as $Mn(NO_3)_2$ and 1 mg. U as $UO_2(NO_3)_2$ was treated by P. 61: the filtrate was tested for uranium by *P. 58*d*: a good test for uranium was obtained.

Thallium.—15 mg. Tl as $Tl(OH)_3$ were treated by P. 61: no precipitate separated. 200 mg. Mn as $MnCl_2$ and 1 mg. Tl as $TlCl_3$ were treated by this procedure. The filtrate was tested for thallium by the regular procedure: a good test was obtained. The precipitate was dissolved in HCl (1.12) and treated by *P. 65*a–d*: a very small precipitate of TlI was obtained, which was estimated to contain not more than 0.1 mg. Tl, showing that thallium is not carried down with the manganese.

The Test for Titanium with H_2O_2 in the Presence of Iron, Cobalt, or Nickel.—500 mg. Fe as $FeCl_3$ were evaporated with a large excess HNO_3 (1.42) to 5 cc.; the dark red solution was diluted to 40 cc.: it became almost colorless. The solution was divided into two parts, and to one of these 0.5 mg. Ti as $TiCl_4$ solution was added; to both parts 2 or 3 cc. H_2O_2 were added: in both a deep yellow color very clearly indicated the presence of titanium.—The experiment was repeated, except that the HNO_3 solution was diluted to about 15 cc.: the test for titanium was distinct, although the ferric solution was not quite colorless.

500 mg. Co as $Co(NO_3)_2$ were evaporated with excess HNO_3 (1.42) to 5 cc.; the red solution was diluted to 15 cc. and divided into two parts, to one of which 1 mg. Ti was added: 2 cc. 3 per cent. H_2O_2 were added: the solution containing titanium acquired a reddish color of a distinct yellow tinge.

The experiment was repeated with 500 mg. Ni as $Ni(NO_3)_2$: the green color of the nickel solution containing titanium changed to olive when the H_2O_2 was added.

P. 62, N. 1: Confirmatory Test for Manganese with Lead Dioxide.—To 1 g. PbO_2 and 10 cc. HNO_3 (1.20) in a casserole were added in separate experiments 0.5, 0.2, 0.1 and 0.02 mg. Mn as $MnCl_2$. The mixtures were boiled gently for about 2 minutes, in covered casseroles, and then poured into test tubes: after the PbO_2 had settled, the color of $KMnO_4$ could be clearly seen, even in the last experiment.—The experiment was repeated without adding $MnCl_2$: a perfectly colorless solution was obtained. —The series of experiments was repeated, except that HNO_3 (1.42) was used: the color of $KMnO_4$ was easily distinguished in each case, but was not so pronounced as with the more dilute acid. Moreover, on standing the pink color faded slowly in the concentrated HNO_3.

To determine whether the test would be satisfactory when the manganese was initially present as MnO_2, 1 mg. Mn as $MnCl_2$ was treated by P. 61, and the precipitate collected on an asbestos filter. About 1/10 of it (*i. e.*, 0.1 mg. Mn) was treated by P. 62: the permanganate color was very distinct.

**P. 62a, N. 1: Separation of Titanium and Zirconium from Manganese by Ammonia.*—To a mixture containing 50 mg. Mn and 50 mg. Ti as nitrates and 4 cc. HCl (1.12) in 50 cc. was added NH_4OH (0.96) very carefully until the mixture was barely alkaline to litmus paper: a white precipitate formed. 2 drops more NH_4OH (0.96) were added, and the mixture was heated on a steambath for 10 minutes: the precipitate remained white. The solution was filtered. The filtrate was tested for titanium by adding more ammonia: no more precipitate separated at once, showing that the precipitation of the titanium was complete. The precipitate was dissolved in hot HCl, the process was repeated, and the filtrate was tested for manganese by adding $(NH_4)S_2$: a precipitate estimated to contain 3 or 4 mg. Mn separated. The titanium precipitate was again dissolved and treated in the same way: no manganese was found in the filtrate, showing that the manganese had been completely removed in two separations.—The experiment was repeated except that the 2 drops of ammonia in excess were not added: only about 2/3 of the titanium precipitated.—The experiment was

repeated, except that NH_4OH was added until the odor after shaking was distinct: the NH_4OH precipitate was brown, showing the presence of a large amount of manganese.—The last experiment was repeated, except that 15 g. NH_4Cl were also added: the NH_4OH precipitate was white, and contained only about 1 mg. Mn.—These experiments prove that a satisfactory separation is obtained only when the hydroxide-ion concentration is very small.

A solution containing 500 mg. Mn and 1 mg. Ti as nitrates, and 10 cc. HCl (1.12) in 60 cc. was made barely alkaline to litmus paper by means of NH_4OH (0.96), an excess of two drops NH_4OH was added, and the mixture was heated for 10 minutes on a steambath: the precipitate was dark colored. The precipitate was dissolved in hot HCl and the separation repeated: a small white precipitate resulted, which was practically free from manganese. It was dissolved in HCl, and a little 3 per cent. H_2O_2 was added: the solution became deep yellow, showing the presence of titanium.—The experiment was repeated with 500 mg. Mn and 2 mg. Zr as nitrates: the results were the same. The final white precipitate was dissolved in hot HCl, the solution was evaporated to a few drops, and a piece of turmeric paper was dipped in it and dried over a small flame: it turned pink, proving the presence of zirconium.

Separation of Zirconium from Manganese by Ammonium Acetate.—A solution of 500 mg. Mn and 5 mg. Zr in 10 cc. HCl (1.12) was just neutralized with NH_4OH; 2 cc. 30 per cent. acetic acid were added, the mixture was diluted to 50 cc., 6 cc. 50 per cent. ammonium acetate were added, and the mixture was boiled: the precipitate was brown, showing that several milligrams of manganese were present and that the separation was unsatisfactory.

Complete Precipitation of Thallium by Ammonium Hydroxide.—20 mg. Tl as Tl_2SO_4 were treated with HNO_3 and $HClO_3$ by P. 61, and then with NH_4OH by P. 64: a dark red flocculent precipitate separated. This was filtered off, the filtrate was evaporated nearly to dryness and tested for thallium with KI by *P. 65*d*: no precipitate of TlI separated, showing that thallium had been completely precipitated by the NH_4OH. Since thallous hydroxide is soluble, it follows also that thallous compounds are completely oxidized by HNO_3 and $HClO_3$ in P. 61.

P. 64, N. 2: Action of Nitric Acid on Potassium Sulphocyanate.—In each of a number of test-tubes 1 cc. HNO_3 (1.42) was placed; varying amounts of water (from 0 to 15 cc.) and finally 5 cc. 10 per cent. KSCN solution were added: in each case a red color appeared slowly in the cold, more quickly on warming slightly, and more quickly in the more concentrated HNO_3 solutions. The red solutions were boiled in casseroles: the color disappeared quickly, and the solutions remained colorless on cooling. More KSCN was added: the color reappeared quickly.—The experiments were repeated with 0.1 mg. Fe as $FeCl_3$: a red color appeared at once in the cold, but on boiling, this color also disappeared in a minute or two. To one of these colorless solutions, after cooling, was added KSCN: the red color appeared at once. To another was added 0.1 mg. Fe as $FeCl_3$: the solution remained nearly colorless.—These experiments show that on boiling with HNO_3, the KSCN is completely decomposed, and therefore that the red color due to nitrous acid cannot be eliminated by boiling.

P. 65, N. 2, 5 and 6: Precipitation of Titanium, Zirconium, and Thallium in the Ammonium Acetate Procedure.—0.5 mg. Ti as $TiCl_4$ in 100 cc. was treated by P. 65: a small precipitate separated, which was proved to contain titanium by *P. 65*b*.—The experiment was repeated with 10 and with 500 mg. Ti; the filtrates were tested for titanium by evaporating with a little H_2SO_4 to fuming, cooling and adding H_2O_2: no color appeared.

A mixture containing 500 mg. Fe as $FeCl_3$ and 20 mg. Zr as $ZrCl_4$ was treated by P. 65: a large amount of zirconium was found in the precipitate, but on adding NH_4OH

to the filtrate a white precipitate was obtained which was estimated to contain 3 to 5 mg. Zr.—10 mg. Zr as nitrate in HNO_3 solution were treated by P. 65, except that no $FeCl_3$ was added; NH_4OH was added only until a very small precipitate of zirconium hydroxide separated and the solution was still acid when the ammonium acetate was added; the filtrate from the basic acetate precipitate was made alkaline with NH_4OH to test for zirconium: a white precipitate separated, which was estimated to contain 1 or 2 mg. Zr.—The experiment was repeated with 1 and 2 mg. Zr, except that NH_4OH was added until the solution was neutral; the filtrate was made acid, evaporated to 20 cc. and then made alkaline with NH_4OH: no precipitate separated.—The last experiment was repeated with 5 mg. Zr as nitrate and 20 mg. PO_4 as Na_2HPO_4: no zirconium was found in the filtrate.—For the fact that zirconium is not precipitated in the presence of considerable acetic acid, and that it then prevents the complete precipitation of titanium, see Hillebrand, *Bull. U. S. Geol. Survey*, **176**, 72 (1900).

20 mg. Tl as $TlCl_3$ were treated by P. 65, except that no $FeCl_3$ was added: a brown precipitate separated on boiling and also on adding NH_4OH; the former was two or three times as large as the latter, thus showing that at least 5 mg. Tl were not precipitated till the NH_4OH was added. The filtrate was evaporated nearly to dryness; H_2SO_4 was added, and the solution when cold was tested for thallium with KI and Na_2SO_3 by *P. 65*d*: a small precipitate of TlI was obtained which was estimated to contain 0.5 to 1 mg. Tl.—The experiment was repeated with 1 mg. Tl: no precipitate resulted on boiling, nor on adding NH_4OH. The filtrate was proved to contain the thallium.—The experiment with 1 mg. Tl was repeated, $FeCl_3$ being added as directed in the procedure: no precipitate separated on adding NH_4OH to the filtrate. Both precipitate and filtrate were tested for thallium: about half of the thallium was found in the precipitate and the remainder in the filtrate.—The last experiment was repeated with 0 5 mg. Tl: a small but distinct test was obtained for thallium both in the precipitate containing the iron and in the filtrate.

P. 65a, N. 1 to 3: Extraction of $FeCl_3$ by Ether.*—See Rothe, *Stahl und Eisen*, **12, 1052 (1892); **13**, 333 (1893); Langmuir, *J. Am. Chem. Soc.*, **22**, 102 (1900); Kern, *J. Am. Chem. Soc.*, **23**, 689 (1901).

To determine the best concentration of HCl to use in this extraction, a series of experiments was performed as follows: 500 mg. Fe as $FeCl_3$ were dissolved in 30 cc. HCl of known specific gravity and this solution was treated several times with about 35 to 40 cc. ether in a separating funnel as described in the procedure. The amount of $FeCl_3$ extracted in each treatment was estimated by evaporating the ether extract to dryness, adding HCl, and precipitating with NH_4OH. The results are given in the following table. Since the ether used contained initially no HCl, the amount of HCl in the water layer is somewhat decreased in each treatment. The proportion of $FeCl_3$ extracted in each treatment was 4 to 5 per cent. with 8 per cent. HCl (sp. gr., 1.04); 95 to 96 per cent. with 18 per cent. HCl (sp. gr., 1.09); 99 per cent. with 22 per cent. HCl (sp. gr., 1.11); and 94 per cent. with 25 per cent. HCl (sp. gr., 1.125).

With the 22 per cent. acid (sp. gr., 1.11) the first extraction took out nearly all the $FeCl_3$ (495 mg. Fe), the second extraction nearly all of 5 mg. Fe remaining, and the third only a fraction of a milligram. A similar result was obtained when 500 mg. Fe as $FeCl_3$ were precipitated with NH_4OH, the precipitate dried between filter papers, and dissolved in HCl (1.12). This result is in agreement with that of Rothe, who recommends an acid of sp. gr. 1.100 to 1.105, for he shook his ether with HCl of this strength before making the separation.

Molecular Formula of Ferric Chloride in Ether Solution.—See Beckmann, *Z. physik. Chem.*, 46, 860 (1903).

Extraction of Thallic Chloride by Ether.—15 mg. Tl as $Tl(OH)_3$ were treated by *P. 65*a*: the solution of $TlCl_3$ in HCl (1.12) had a yellow color, but this layer was colorless after it was shaken with ether; the ether layer had a yellowish color. The first ether extract contained nearly all the thallium, the second ether extract contained less than 1 mg., and the water layer after the two extractions was practically free from thallium.

**P. 65a, N. 4: Behavior of Titanium, Zirconium, and Uranium in the Ether Treatment.*—A solution of 50 mg. Ti as $TiCl_4$ in one experiment, and of 50 mg. Zr in another, in 30 cc. HCl (1.11) was shaken with an equal volume of ether; the ether layer was evaporated to dryness in a casserole on a waterbath, HCl (1.20) was added and heated, the solution was made alkaline with NH_4OH: no precipitate separated in either case, showing that no titanium or zirconium had dissolved in the ether layer. In the case of titanium the water layer became reddish yellow owing to the presence of H_2O_2 in the ether, and in the case of zirconium a white precipitate ($ZrCl_4$?) separated in the water layer, but when the ether was expelled by evaporation a clear solution resulted. A white precipitate was also found to result with titanium in an experiment in which 300 mg. PO_4 were also present.

For proof that uranium is not extracted, see Kern, *J. Am. Chem. Soc.*, 23, 689 (1901).

**P. 65a, N. 5: Extraction of Iron by Ether in the Presence of Phosphate.*—500 mg. Fe as $FeCl_3$ and 300 mg. PO_4 as ammonium phosphate were dissolved in 30 cc. HCl (1.09) and treated with ether (35 cc.) as described in the procedure: about 95 per cent. of the iron was extracted in each treatment and the phosphate remained in the water layer.

**P. 65b, N. 1: Nature of the Compound of Hydrogen Peroxide with Titanium.*—In regard to the colored solution, and the preparation of solid TiO_3, see Schönn, *Z. analyt. Chem.*, 9, 41 (1870); Classen, *Ber.*, 21, 370 (1888); Levy, *Ann. chim. phys.* (6) 25, 463 (1892); Melikoff and Pissarjewsky, *Ber.*, 31, 953 (1898).

Mr. Chas. Field, 3rd, working in this laboratory, performed the following migration experiment. A colored solution was prepared by rotating for three hours pure TiO_3, which had been dried over P_2O_5, with a normal HNO_3 solution which contained 1 mol. H_2O_2 per liter. The resulting solution was 0.087 molal with respect to TiO_3. A large U tube which was partly filled with normal HNO_3 solution was placed in a thermostat at 25° and the titanium solution was carefully introduced through a tube at the bottom of the U. The surfaces of contact of the two solutions were sharply marked. After a current had passed for 8 hours, one of the surfaces of the red solution had moved 4 cm. upward toward the cathode, and the other boundary had moved away from the anode a nearly equal distance. This proves that the color is due to a cathion containing titanium.

Delicacy of the Hydrogen Peroxide Reaction for Titanium.—0.1 mg. Ti as chloride was treated by *P. 65*b*: a distinct yellow color appeared on adding the H_2O_2 solution.

**P. 65b, N. 2: Precipitation and Separation of Titanium and Zirconium as Phosphate.*—See Hillebrand, *Bull. U. S. Geol. Survey*, 176, 75 (1900).

0.5 and 1 mg. Zr and a mixture of 1 mg. Zr and 100 mg. Ti as chloride were treated by *P. 65*b*: flocculent precipitates formed in every case within 10 minutes but were more distinct after half an hour.—100 mg. Ti alone were treated by *P. 65*b*: no precipitate separated in several hours.

10 mg. Zr as chloride were treated by *P. 65*b*: the precipitate was filtered off after half an hour, and the filtrate made alkaline with NH_4OH: a small precipitate estimated

to contain about 0.3 mg. Zr separated. The result was the same when the filtration was made after 20 hours.—The experiment was repeated, except that only 3 or 4 cc. phosphate solution were used: the filtrate contained 0.5 to 1.0 mg. Zr after half an hour and after 1 hour.—The experiment was repeated, using about 15 cc. phosphate solution; only 0.1 to 0.2 mg. Zr remained in the filtrate after 2 hours.

To a number of solutions, containing 1 mg. Zr as chloride and varying amounts of H_2SO_4 (1.20) in 15 cc., were added 5 cc. 7 per cent. $Na_2HPO_4.12H_2O$ solution: with 1 and 2 cc. of acid the solutions became turbid at once, and flocculent precipitates settled out within 20 minutes; with 5 cc. acid the solution remained clear for about 10 minutes, but after 1 hour there was a distinct precipitate; with 10 cc. acid the solution remained clear for a longer time and only a minute precipitate separated in 1.5 hours.

Precipitation of Titanium with Zirconium Phosphate.—10 mg. Zr and 10 mg. Ti as chlorides were treated by *P. 65*b*: the precipitate when collected on a filter was distinctly yellow and this color remained after washing with water for an hour. About 10 cc. 15 per cent. HF solution were poured through the filter in a celluloid funnel and the solution was treated again by *P. 65*b*: the phosphate precipitate was white, and the titanium in the solution was estimated from the color to be about 1 mg.—0.1 mg. Ti and 100 mg. Zr as chlorides were treated by *P. 65*b*: the solution became distinctly yellow on adding H_2O_2, and the filtrate from the phosphate precipitate was also yellow, showing that titanium is not completely carried down by the zirconium. (100 mg. Zr alone gave no color with H_2O_2.)

**P. 65b, N. 3: Precipitation of Thorium as Phosphate.*—2, 5, and 50 mg. Th as nitrate were treated by *P. 65*b*: white gelatinous precipitates separated on the addition of Na_2HPO_4, the precipitate being small and forming slowly in the experiment with 2 mg. Th. In the experiment with 5 mg. a 10 cc. portion of HF (1 volume 45 per cent. HF to 2 volumes water) was poured several times through the filter; the solution was evaporated with H_2SO_4 to fuming, cooled, diluted and excess NH_4OH added: no precipitate separated at once and only a very small one on standing an hour.

**P. 65b, N. 4: Behavior of Manganese, Cobalt, Uranyl and Vanadyl Salts in the Tests for Titanium and Zirconium.*—100 mg. Mn as $MnCl_2$ were treated by *P. 65*b–c*: with H_2O_2 no color resulted, and no precipitate formed when Na_2HPO_4 was added, nor on standing 1 hour. After the addition of just sufficient powdered Na_2SO_3 to reduce the H_2O_2 (determined by testing portions of the solution with Ti solution), no precipitate formed, but when about 1 g. more Na_2SO_3 was added a large precipitate separated.—The experiment was repeated separately with 100 mg. Co as $CoCl_2$ and with 5 mg. U as $UO_2(NO_3)_2$: there was no change of color with H_2O_2 and no precipitate with Na_2HPO_4 on adding enough Na_2SO_3 to destroy the H_2O_2.—The experiment was repeated with 100 mg. U as $UO_2(NO_3)_2$: the solution was distinctly yellow before the H_2O_2 was added, and a large white precipitate formed on adding just sufficient Na_2SO_3 to decompose the H_2O_2.

10 and 100 mg. V as Na_3VO_4 were treated in separate experiments by *P. 65*b–c*: with the 10 mg. the color obtained on adding H_2O_2 was similar to that obtained with 3 to 5 mg. Ti; with the 100 mg. however the color was of a much redder shade than that with titanium; on the addition of an excess of Na_2SO_3 the color changed at once to blue, showing the presence of a vanadyl salt, and no precipitate had separated in either case after several hours in the cold or on boiling.

**P. 65c, N. 1: Behavior of Titanium in Acid Solutions towards Sodium Phosphate.*—To a solution containing 0.5 mg. Ti as chloride and 2 cc. H_2SO_4 (1.20) in 10 cc. were added 10 cc. 7 per cent. $Na_2HPO_4.12H_2O$ solution: the solution remained clear for 10 minutes, but had become distinctly turbid in half an hour. Several solutions,

containing 10 mg. Ti as chloride and varying amounts of H_2SO_4 (1.20) were treated in the same way; the flocculent precipitates were filtered off after 10 minutes, and the filtrates were made alkaline with NH_4OH: in the experiment with 2 cc. acid the filtrate contained 0.5 to 0.1 mg. Ti; in that with 3 cc. acid, 1 to 3 mg. Ti; in the experiment with 5 cc. acid, 3 to 4 mg. Ti.

10 mg. Ti as chloride were treated by *P. 65*b–c*, and after half an hour the mixture was filtered, and the filtrate made alkaline with NH_4OH: a very small precipitate was obtained containing about 0.5 mg. Ti.—The experiment was repeated with 0.5 mg. Ti: the solution became distinctly turbid on decolorizing with H_2SO_3. Half of the turbid solution was heated to boiling: a distinct, flocculent precipitate was obtained. The other half was allowed to stand in the cold for half an hour: the precipitate in this case also became somewhat flocculent.

**P. 65d, N. 1: Test for Thallium with KI.*—0.5, 0.2, and 0.1 mg. Tl as Tl_2SO_4 were treated by *P. 65*d*, the total volume being about 10 cc.: a distinct yellow finely divided precipitate of TlI was obtained in each experiment, even in that with 0.1 mg. Tl. For proof that 500 mg. ferric iron does not interfere with the test, see T. A., No. 174–6.

**P. 65d, N. 3: Flame Test for Thallium.*—0.5, 0.2, and 0.1 mg. Tl were precipitated by *P. 65*d* as TlI. The precipitates were collected on small filters and washed twice with a very little water. The moist filter was removed from the funnel, a looped platinum wire was drawn across its surface to collect a little of the precipitate, and introduced into a colorless gas flame: with 0.5 mg. Tl, the momentary green color was generally seen, but it was sometimes obscured by the yellow flame, due to sodium and to small fibers of paper; with 0.2 and 0.1 mg. Tl the green color could not be detected with certainty.—The experiments were repeated, except that the TlI precipitates were collected on hardened filters: the green flame was much more brilliant with 0.5 and 0.2 mg. Tl than in the corresponding experiments with ordinary filter paper; it could, however, scarcely be seen with 0.1 mg. Tl.

P. 69, N. 1: Potassium Cobaltic Nitrite.—See Fisher, *Pogg. Ann.*, 74, 115 (1848); Sadtler, *Am. J. Sci.* (2), 49, 196 (1870); Rosenheim and Koppel, *Z. anorg. Chem.*, 17, 35 (1898).

P. 69, N. 2: Precipitation of Cobalt with Potassium Nitrite.—0.1 and 0.3 mg. Co as $CoCl_2$ were treated by P. 69: in each experiment the solution became distinctly turbid within 5 minutes.—The experiment was repeated in the absence of cobalt: the solution remained perfectly clear.—For the detection of 0.5 mg. Co in the presence of 250 mg. Ni in P. 69, see T. A., No. 127.

500 mg. Co as nitrate were treated by P. 69: the mixture was shaken well, allowed to stand, and filtered after about half an hour, and again allowed to stand: a considerable precipitate again separated.—The experiment was repeated except that the mixture was heated on a waterbath to 50 or 60° with frequent shaking for half an hour; it was allowed to cool and filtered: no precipitate separated in the filtrate even on standing over night.

Separation of Nickel from Cobalt with Potassium Nitrite.—500 mg. Co and about 5 mg. Ni as nitrates were treated by P. 69; after standing 20 hours the mixture was filtered; the filtrate was evaporated almost to dryness with HCl, and made alkaline with NaOH: only a very small green precipitate separated corresponding to not more than 2 mg. Ni. Half of the cobalt precipitate obtained was treated by P. 70: a very good test for nickel was obtained.—The experiment was repeated except that the mixture was heated on a waterbath for half an hour: less nickel was found in the filtrate than in the preceding experiment.

Precipitation of Potassium Nickelous Nitrite.—250 mg. Ni (previously freed from

cobalt by a KNO_2 treatment) were treated by P. 69, except that the volume was cut down to 50 cc. without however altering the total amounts of reagents used: a distinct reddish colored precipitate separated within 20 minutes which was proved to contain nickel but no cobalt by the borax bead test.—For the action of HNO_2 on nickel salts and the formation of $K_4Ni(NO_2)_6$ see Lang, *J. prakt. Chem.*, **86**, 299 (1862); Hampe, *Lieb. Ann.*, **125**, 346 (1863); and Reichard, *Chem.-Ztg.*, **28**, 479, 885, 912 (1904).

P. 70, N. 2: Delicacy of Hypobromite Test for Nickel.—150 mg. Co free from nickel were treated by P. 70: no precipitate was observed, not even on filtering. The experiment was repeated except that 0.15 mg. Ni as $NiCl_2$ was added: the solution became dark colored on adding excess NaBrO, but no precipitate collected; it was easily seen, however, on the filter.—0.2 mg. Ni as $NiCl_2$ was treated by P. 70: a distinct precipitate was obtained on filtering.

Separation of Nickel from Cobalt by Hypobromite.—200 mg. Co and 0.5 mg. Ni as chlorides were treated by P. 70; the precipitate was tested for cobalt in the borax bead: no blue color was obtained.

A large number of experiments were performed to determine the proper conditions for making this separation. In working with cobalt free from nickel, it was found that a precipitate of $Co(OH)_3$ always formed when the NaBrO reagent (or bromine water and NaOH) was added very soon after the addition of KCN, and that the necessary interval of time was greatly shortened by increasing the excess of KCN added.

The following experiments show that excess of NaBrO is essential to the precipitation of nickel. 1 mg. Ni as $Ni(NO_3)_2$ was treated by P. 69; the NaBrO solution was added in small portions and after the addition of each portion the solution was tested with the starch KI paper: as long as this paper remained colorless no precipitate of $Ni(OH)_3$ separated, but after the precipitate formed the paper became blue when dipped into the mixture.—The experiment was repeated with 10 mg. Ni. As long as the precipitation was incomplete the paper remained colorless, or only a small brown ring was formed on the paper, but after complete precipitation all of the paper immersed in the solution became brown or blue.

P. 70, N. 4: Action of H_2S on Alkaline Tartrate Solutions Containing Nickel or Cobalt.—Villiers, *Compt., rend.* **119**, 1263 (1894); **120**, 46 (1895), found that when H_2S was passed into a NaOH containing freshly precipitated $Ni(OH)_2$ (but no tartrate) the hydroxide was quickly converted into black nickel sulphide, but that a portion of the nickel passed into solution giving a deep brown color, proving that the presence of tartrate is not essential for the formation of the brown solution.—0.5 mg. Ni as nitrate was treated by both parts of P. 70: a deep brown solution was obtained on saturating the alkaline tartrate solution in a test tube with H_2S.—0.1 and 0.2 mg Ni as nitrate were dissolved in a little HNO_3 and treated by the second paragraph of P. 70, about 5 cc. of 10 per cent. tartaric acid and 5 cc. excess of NaOH being added: clear dark yellow solutions were obtained on saturating with H_2S.—The experiment was repeated with 1 mg. Ni: on passing in H_2S the solution remained nearly colorless for about 1 minute, but finally a clear dark brown solution resulted.—The experiment was repeated with 20 mg. Ni: on saturating with H_2S the liquid in the test-tube was opaque and almost black in color. The liquid was filtered: very little precipitate remained on the filter. It was allowed to stand several hours: a black precipitate separated but the filtrate was still black and opaque.

20 mg. Co as $CoCl_2$ in a little dilute HNO_3 were treated by the second paragraph of P. 70: a black precipitate separated as soon as the H_2S was led in and the cobalt was completely precipitated within 1 minute. The mixture was filtered, the filtrate was saturated with H_2S, and the test-tube corked and set aside: the solution remained colorless for several hours. A similar solution was exposed to the action of the air

in an open flask: it became dark yellow in about 1 hour owing to oxidation of the sulphide and consequent formation of polysulphide.—The experiment was repeated except that 1 mg. Ni as $NiNO_3$ was also present; the excess of 10 per cent. NaOH was 4 or 5 cc.; H_2S was led into the solution for about 1 minute and the CoS filtered off: the filtrate was nearly colorless. This was saturated with H_2S: it became brown, the color being such as to indicate that very little of the nickel had been carried down with the cobalt.—This experiment was repeated except that the H_2S was led through the solution for 5 minutes before the CoS was filtered off: the filtrate was of a lighter brown than before, indicating that over half the nickel had been carried down with the cobalt.—The experiment was repeated except that the CoS was not filtered off till after 10 minutes: the filtrate was almost colorless, and remained so on saturating again with H_2S.—The experiment was repeated, the CoS being filtered off after half an hour: the filtrate was colorless and contained no nickel.—In a similar series of experiments in which a smaller excess of NaOH than 4 to 5 cc. was added, the filtrate was light brown after 1 minute, and nearly colorless after 5 minutes, thus showing that there is more danger of losing nickel when the excess of alkali is small, in which case the brown solution is formed more quickly.—This result that NiS is deposited on CoS after the separation of the latter was confirmed by several experiments.

Similar experiments were made with a mixture of 20 mg. Fe as $FeCl_3$ and 1 mg. Ni, and with one of 20 mg. Mn and 1 mg. Ni: good tests for nickel were obtained in both cases.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE CARRYING DOWN OF SOLUBLE OXALATES BY OXALATES OF THE RARE EARTHS.

BY GREGORY PAUL BAXTER AND HERBERT WILKENS DAUDT.

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In a recent investigation[1] it has been shown that neodymium oxalate, when precipitated in neutral or nearly neutral solution by means of ammonium oxalate, carries down considerable quantities of this salt, and that the amount carried down increases with increasing concentration of molecular ammonium oxalate at the moment of precipitation. Furthermore, it was shown that neodymium oxalate has no tendency to carry down molecular oxalic acid, and that occlusion of ammonium oxalate may be prevented by diminishing the molecular concentration of the latter salt with a strong acid before precipitation. Other rare earth oxalates were found to exhibit a like tendency to occlude ammonium oxalate. Since it seemed probable that the carrying down of sodium and potassium oxalates[2] would vary with conditions of precipitation in a similar manner, the following investigation was undertaken to test this point.

The method employed was to precipitate the rare earth oxalate under different conditions, and to analyze the precipitated oxalate by deter-

[1] Baxter and Griffin, THIS JOURNAL, 28, 1684 (1906).

[2] The well-known fact that the oxalates of the alkalis are carried down by the oxalates of the rare earths was first noted by Sheerer. Pogg. Ann. [2], 56, 496 (1842).

mining the ratio of metallic oxide to C_2O_3. The atomic weight of the metal being known, the excess of C_2O_3 could be calculated and hence the purity of the precipitate. Although all the rare earth oxalates contain crystal water, even after drying at an elevated temperature, the amount of this water is immaterial for the purpose in hand.

Since none of the rare earth specimens were pure, it was necessary to determine the average atomic weight of each specimen. This was done by the oxalate method first proposed by Stolba.[1] A hot solution of oxalic acid containing a small quantity of nitric acid was slowly added with constant stirring to a hot nitric acid solution of the rare earth until precipitation was complete. After the precipitate had been washed ten times by decantation with hot water, it was collected upon a porcelain Gooch crucible provided with a disk of filter paper in place of an asbestos mat, and was dried in an electric air-bath at about 125° for twenty-four hours. Shortly before being weighed out for analysis, the dried precipitates were thoroughly mixed by grinding in an agate mortar to insure uniformity in water content,[2] and all portions of the same material were weighed out at the same time, in order to avoid error from hygroscopicity.

The per cent. of oxide in the oxalate was determined by igniting weighed portions of about one-half gram in platinum crucibles, while the ratio C_2O_3: oxalate was found by dissolving weighed amounts of the oxalate in hot 2 *N* sulphuric acid and titrating the oxalic acid with standard potassium permanganate. From the ratio $M_2O_3 : 3C_2O_3$ the average atomic weight of the sample was calculated, the following atomic weights being assumed: H = 1.008, O = 16.00, C = 12.00.

The permanganate solution was standardized with oxalic acid which had been allowed to come to constancy over sulphuric acid of the specific gravity 1.35. This oxalic acid had been three times recrystallized, with centrifugal drainage. Although the permanganate solution changed in concentration very slowly, re-standardization was carried out frequently.

In order to gain some idea of the extent to which the alkali oxalates are carried down by the rare earth oxalates under conditions most favorable for this effect, each material under investigation was precipitated by pouring a hot nearly neutral solution of the nitrate of the rare earth into a hot solution of from three to four times the equivalent quantity of each alkali oxalate. In this precipitation the solution of the rare earth nitrate was on an average about four-tenths normal and the solution of the alkali oxalate about six-tenths normal.

Next the same material was again precipitated in as nearly as possible

[1] Sitzber. böhm. Ges., Dec., 1878; also Chem. News, 41, 31 (1880).

[2] Gibbs, Proc. Amer. Acad., 28, 262 (1893).

the same way, except that about twice the equivalent quantity of nitric acid was added to the solution of the alkali oxalate before the precipitation. Although the dissociation of the first hydrogen of oxalic acid is very considerable,[1] that of the second hydrogen is small.[2] Hence, in the presence of a high concentration of the hydrogen ion the concentration of the oxalate ion and therefore that of the molecular alkali oxalate must be very low, so that little carrying down of the alkali oxalate is to be expected.[3]

With solutions as concentrated as the above it is of course probable that a small amount of soluble oxalate would be "included" in cells of mother liquor in the highly crystalline precipitates. This may be the reason for at least a portion of the small amount of alkali oxalate found even in precipitates formed by methods calculated to reduce occlusion to a minimum.

As in the previous investigation, the first element studied was neodymium. The sample used was not quite pure, its absorption spectrum showing, besides the bands of neodymium, traces of those of samarium and praseodymium. Other elements giving no absorption spectrum may have been present. The average atomic weight of the sample was found by analysis of the oxalate as described above.

ATOMIC WEIGHT.

	I.	II.	III.	IV.	Average.
Per cent. of Nd_2O_3	53.87	53.81	53.77	.....	53.82
Per cent. of C_2O_3	34.29	34.36	34.30	34.37	34.33

Ratio $M_2O_3 : 3C_2O_3 = 1.5677$. $M = 145.3$.

Although the average atomic weight of the sample is only slightly higher than the most probable atomic weight of neodymium, 144.5,[4] this result does not indicate with exactness the purity of the sample, for the atomic weights of the known impurities, praseodymium and samarium, lie on opposite sides of that of neodymium. The specimen undoubtedly consisted chiefly of neodymium, however.

A portion of the same material was next precipitated by pouring a hot nearly neutral solution of the nitrate into a hot solution of about three times the equivalent quantity of potassium oxalate. Portions of the carefully washed and dried precipitate, when held in the Bunsen flame, indicated the presence of considerable quantities of potassium. A fruitless attempt to expel all the potassium by prolonged ignition in the flame of a blast lamp, showed that some other method was necessary

[1] Ostwald, Z. physik. Chem., 3, 281 (1889).

[2] *Ibid.*, 9, 553 (1892).

[3] In the previous paper the effect of increasing the hydrogen ion concentration was erroneously imputed to the formation of molecular oxalic acid instead of the acid oxalate ion.

[4] v. Welsbach, Sitzb. Akad. Wiss. Wien, 112, 1037 (1904).

for the determination of the neodymium oxide. Accordingly, weighed amounts of the precipitate were first dissolved in either sulphuric or nitric acid, and, after the solution had been neutralized with freshly distilled ammonia, ammonium oxalate was added until precipitation appeared complete. More ammonia was then added until the solutions were slightly ammoniacal. After standing some time, the precipitates were washed several times with hot water, filtered, ignited and weighed. Occluded ammonium oxalate was, of course, volatilized during ignition. The oxalic acid was determined as before described.

NEUTRAL PRECIPITATION WITH POTASSIUM OXALATE.

	I.	II.	III.	Average.
Per cent. of Nd_2O_3	46.76	46.76	46.70	46.74
Per cent. of C_2O_3	37.71	37.61	37.66	37.66
Per cent. of C_2O_3 equivalent to 46.74 per cent. of Nd_2O_3	.....	.....	.....	29.82
Excess per cent. of C_2O_3	.....	.....	.....	7.84
Per cent. of $K_2C_2O_4$ carried down	.....	.....	.....	18.10

The experiment with potassium oxalate was then repeated with similar solutions except that the potassium oxalate solution before precipitation was made acid with about twice the equivalent amount of nitric acid. It has already been shown that neodymium oxalate shows no tendency to carry down oxalic acid.[1] This new precipitate of neodymium oxalate gave no visible flame test for potassium, and analysis showed only 0.30 per cent. of potassium oxalate to have been carried down. The per cent. of neodymium oxide was found by ignition of weighed portions of the oxalate, finally with a blast lamp to expel traces of potassium. This method is later shown to give accurate results in the case of a precipitate formed with sodium oxalate.

The result of this experiment, in which the carrying down of potassium oxalate is a little less than two per cent. as large as in neutral solution, is in accord with the prediction, and also with the behavior of neodymium oxalate with ammonium oxalate previously observed, the excess of oxalate found not being greater than could be accounted for on the basis of inclusion.

When sodium oxalate in neutral solution was used as precipitant, the neodymium solution being added to a large excess of oxalate, the dried precipitate gave scarcely any flame test for sodium. The same surprising result was obtained in two successive repetitions of the experiment. One of the precipitates, upon analysis, proved to contain only a few tenths of a per cent. of sodium oxalate. The analyses for neodymium oxide were made by ignition of the oxalate with a blast lamp.

[1] Baxter and Griffin, *Loc. cit.*

In strongly acid solution with sodium oxalate as precipitant, exactly the same proportion of sodium oxalate was found in the precipitate. The neodymium oxide was determined by ignition. In one of the analyses the neodymium oxide, after being weighed, was dissolved in nitric acid and the neodymium was precipitated with ammonium oxalate. The weight of the oxide obtained by ignition of this latter precipitate agreed essentially with that of the original, showing that small quantities of the occluded alkalies may be volatilized completely by ignition.

Since the solubility of the oxalates of the rare earths in nitric acid is a variable one, and since our material was known to be a mixture, at the end of the experiments with neodymium, the average atomic weight of the material which had been through the preceding operations was redetermined, and was found to have diminished 0.3 to 145.0. It is to be noted that the effect of this diminution is to exaggerate slightly the occlusion. With sodium oxalate in acid solution for instance, the per cent. of sodium oxalate carried down, calculated upon the basis of the lower atomic weight, is 0.3 instead of 0.4.

OCCLUSION BY NEODYMIUM OXALATE.

	$K_2C_2O_4$. Per cent.	$Na_2C_2O_4$. Per cent.
Neutral precipitation	18.1	0.4
Acid precipitation	0.3	0.4

Lanthanum upon examination was found to behave similarly to neodymium. The material used was essentially free from elements whose solutions absorb in the visible region, and its atomic weight, determined as in the case of neodymium to be 139.1, was found to be very close to the probable value of this constant, 138.9.

Since the carrying down of ammonium oxalate by lanthanum oxalate was not investigated in the previous research, this point was taken up here. The precipitate formed by adding a nearly neutral solution of lanthanum nitrate to a large excess of ammonium oxalate proved to contain a considerable amount of ammonium oxalate. When, however, the ammonium oxalate solution was acidified with twice the equivalent quantity of nitric acid, only a trace of ammonium oxalate was found.

Similar results were obtained with potassium oxalate as precipitant, this oxalate being carried down in considerable quantities from neutral solution and very slightly from strongly acid solution. In the analyses of the precipitate from neutral solution the lanthanum oxide was determined by igniting weighed portions of the oxalate, leaching the oxide with water and filtering the wash water through a tiny filter, and finally igniting both oxide and filter paper. In analyzing the precipitate from acid solution the lanthanum oxide was determined by ignition only.

When sodium oxalate was used as precipitant, only small quantities

of this substance were found in the precipitates of lanthanum oxalate either from neutral or from acid solution.

OCCLUSION BY LANTHANUM OXALATE.

	$(NH_4)_2C_2O_4$ Per cent.	$K_2C_2O_4$. Per cent.	$Na_2C_2O_4$. Per cent.
Neutral precipitation	5.4	2.3	0.5
Acid precipitation	0.2	0.1	0.8

It is noticeable that the carrying down of both potassium and ammonium oxalates by lanthanum oxalate is very much less than by neodymium oxalate under nearly the same conditions of precipitation.

The third material examined was of somewhat complex nature. A solution of gadolinite earths, which had been treated with potassium sulphate, was fractionated with magnesium oxide until about half the earths remaining had been precipitated. The magnesium oxide fractions, which seemed identical as far as spectroscopic evidence was concerned, were combined and fractionally crystallized from concentrated nitric acid until the greater part of the neodymium and praseodymium had passed into the mother liquors. A portion of this material, which consisted largely of samarium, was used in the following work. Subsequent prolonged fractional crystallization showed the presence of gadolinium, dysprosium, europium and holmium. This material was investigated in exactly the same way as in the cases of neodymium and lanthanum, by precipitating the oxalate in both neutral and acid solution with a large excess of ammonium, potassium and sodium oxalates. The average atomic weight of this material was found to be 149.3.

OCCLUSION BY SAMARIUM OXALATE.

	$(NH_4)_2C_2O_4$. Per cent.	$K_2C_2O_4$. Per cent.	$Na_2C_2O_4$. Per cent.
Neutral precipitation	5.9	20.7	5.9
Acid precipitation	0.0	0.0	0.1

From the preceding table it can be seen that the carrying down of the precipitant in neutral solution and almost absolute purity of the precipitate from acid solution is in accord with the behavior of the elements previously studied—lanthanum and neodymium. It is further to be noted that the quantity of sodium and potassium oxalates found in the precipitates from neutral solution is markedly greater in all cases than was found with neodymium and lanthanum oxalates. This is in accord with the fact that elements of the yttrium and erbium groups in general show marked tendency to form soluble double oxalates with the oxalates of ammonium and the alkalis.

Finally, a sample of yttria was examined in a similar fashion. This sample was very crude, its atomic weight being found to be 102.7.

First, precipitation with potassium oxalate in strongly acid solution was investigated. Considerable quantities of potassium in the precipi-

tate were indicated by a strong flame test. Some difficulty was experienced in the determination of the yttrium oxide in the oxalate, owing to failure of all attempts to reprecipitate the oxalate completely from either neutral or slightly acid solution. The method finally adopted was that of leaching the ignited oxalate with hot water and collecting the small amount of suspended yttrium oxide upon a tiny filter paper, as previously described in the case of lanthanum. Even after filtration the decantate was cloudy, but repeated filtration through the same filter paper removed all but negligible amounts of the yttrium oxide. The washed oxide was dried upon the steam-bath, ignited and weighed, and its weight was added to the weight of oxide upon the filter paper after ignition. The filtrate was alkaline to phenolphthalein. Over seventeen per cent. of potassium oxalate was found.

Since the material had been precipitated in acid solution several times between the original determination of the atomic weight and the acid precipitation with potassium oxalate described above, the change in atomic weight produced by partial solubility of the oxalates in nitric acid was determined, and found to be considerable, the new value for the atomic weight being 104.7. Hence the calculated percentage of potassium oxalate carried down in the above case is probably slightly too low.

The fraction of material used in the above experiments was now mixed with a new portion of the original substance, and the average atomic weight of the mixture was found to be 103.2.

This new material was now precipitated with potassium oxalate in neutral solution under as nearly as possible the same conditions as before. The precipitated oxalate contained potassium oxalate in slightly greater quantities than when formed in acid solution.

Examination of the precipitates formed with sodium oxalate in both neutral and acid solutions showed that in both cases very small quantities of the precipitant were carried down.

Since yttrium oxalate was found to carry down large quantities of potassium oxalate even in strongly acid solution, an experiment was performed to determine whether this was the case with ammonium oxalate also. Baxter and Griffin have already found that yttrium oxalate, when precipitated from neutral solution, may carry down as much as 16.5 per cent. of ammonium oxalate. The precipitate of oxalate from acid solution gave a strong test for ammonia when treated with caustic soda, and was found to contain a somewhat lesser amount of occluded ammonium oxalate than the precipitate formed in neutral solution.

OCCLUSION BY YTTRIUM OXALATE.

	$(NH_4)_2C_2O_4$. Per cent.	$K_2C_2O_4$. Per cent.	$Na_2C_2O_4$. Per cent.
Neutral precipitation	....	18.0	1.0
Acid precipitation	13.6	17.5	0.9

Finally, in order to show conclusively that oxalic acid itself is not carried down by yttrium oxalate, a precipitate was formed by adding a solution of yttrium nitrate to a concentrated solution of a large excess of oxalic acid. Analysis of the precipitate showed not only that no carrying down of oxalic acid takes place but also that the average atomic weight of the material had increased to 106.1. The result of this rise in atomic weight, as previously stated, is to make the carrying down of precipitant appear less than it really is.

Since in all cases previously described the precipitates were formed in hot solution, in order to determine the effect of temperature upon the occlusion, precipitations with neodymium solutions were made at ordinary and at boiling temperatures with solutions otherwise identical. In one case a cold solution of neodymium nitrate was added to a cold saturated solution of a large excess of ammonium oxalate, and in a second case similar solutions were precipitated boiling hot. The precipitate from cold solution gave no test for ammonia when treated with sodium hydroxide and analysis of the precipitate gave no evidence of occlusion, while in the second case 2.1 per cent. of ammonium oxalate was found.

Similar experiments were then carried out with a cold saturated solution of potassium oxalate and with a similar solution at boiling temperature. The precipitate formed at the lower temperature was found to contain 10.0 per cent. of potassium oxalate while the one formed at boiling temperature contained nearly double this proportion, 17.5 per cent.

The effect of high temperature is very marked both with ammonium oxalate and with potassium oxalate. The smaller quantity of ammonium oxalate found even in the hot precipitation is due at least in part to the fact that the solutions of ammonium oxalate were more dilute, owing to the lesser solubility of this salt at ordinary temperatures.

The very considerable extent of the carrying down of the oxalates of the alkalis and ammonium by all the rare earth oxalates investigated, points to the formation of double salts as the cause of the phenomenon rather than to ordinary solid solution. Although the foregoing experiments may not indicate the limiting values of the occlusion under the conditions most favorable and least favorable for the phenomenon, it is interesting to tabulate the molecular ratios between the occluded and occluding oxalates.

A glance at the following table shows that in no case does the carrying down of a soluble oxalate exceed the proportion of one molecule of alkali oxalate to one of rare earth oxalate. One might conclude from this fact that stable insoluble double salts containing more than one

molecule of alkali oxalate to one of rare earth oxalate do not exist, although the grounds for such a conclusion are not by any means final.

MOLECULAR RATIO OF OCCLUDED OXALATE TO RARE EARTH OXALATE.

	$Na_2C_2O_4$.		$K_2C_2O_4$.		$(NH_4)_2C_2O_4$.	
	Acid.	Neutral.	Acid.	Neutral.	Acid.	Neutral.
$Nd_2(C_2O_4)_3$....	0.02	0.02	0.01	0.79	0.01[1]	0.71[1]
$La_2(C_2O_4)_3$.....	0.04	0.02	0.00	0.09	0.01	0.27
$Sm_2(C_2O_4)_3$....	0.00	0.30	0.00	0.94	0.00	0.32
$Y_2(C_2O_4)_3$.....	0.04	0.04	0.69	0.73	0.65	0.82[1]

It is somewhat difficult to explain the unexpected behavior of yttrium oxalate, when precipitated from acid solutions, the occlusion being only slightly diminished thereby. The oxalates of the earths of the yttrium and erbium group, however, show considerable tendency to form *soluble* double oxalates with the oxalates of the alkalis and ammonium, indicating a more marked tendency toward double salt formation than is possessed by the oxalates of the neodymium group. Since even in the presence of a high hydrogen ion concentration the oxalate ion concentration and hence that of alkali oxalate must be appreciable, the carrying down of alkali oxalate is still possible where the tendency in this direction is strong. The fact that the occlusion by yttrium oxalate is not greater in neutral solution may be explained on the hypothesis previously stated that there is no tendency to form insoluble double oxalates containing more than one molecule of alkali oxalate to one of yttrium oxalate.

The following general conclusions seem to be justified from the foregoing results:

(1) The oxalates of the rare earths show marked but varying tendencies to carry down the oxalates of the alkalis and ammonium.

(2) This tendency increases with increasing concentration of molecular alkali oxalate at the moment of precipitation.

(3) Potassium and ammonium oxalates are carried down to a much greater extent than sodium oxalate. Precipitation with sodium oxalate in most cases gives precipitates only slightly contaminated with this substance even in neutral solution.

(4) The carrying down of the soluble oxalates is greater at high than at low temperatures.

(5) By conducting the precipitation in the presence of a quantity of a strong acid considerably more than equivalent to the alkali oxalate, thus very much reducing the concentration of molecular alkali oxalate, the carrying down is in many cases almost wholly prevented. In the case of yttrium, the diminution in occlusion is slight.

(6) In order to produce as pure as possible a precipitate of a rare earth oxalate by means of an alkali oxalate or ammonium oxalate, precipita-

[1] From the results of Baxter and Griffin, *Loc. cit.*

tion should be conducted in cold dilute solution in the presence of a quantity of a strong acid considerably more than equivalent to the oxalate added.

We are greatly indebted to the Welsbach Light Company for some of the rare earth material.

CAMBRIDGE, MASS.,
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YTTRIUM EARTHS.

[FIRST PAPER.]

BY VICTOR LENHER.

Received December 28, 1907.

The methods which we have at our disposal for the separation of the earths of the yttrium group may be classified under the following heads: (1) Fractional precipitation; (2) Fractional crystallization; (3) Fractional decomposition of such salts as the nitrates by heat.

Under fractional precipitation, we have methods which depend largely on the differences in basic properties, such as the fractional precipitation by ammonia, magnesia, etc. The speed by which separations are effected by use of this principle depends largely on how quickly the system can be brought into equilibrium.

In the methods of fractional crystallization we must depend necessarily on the differences in solubility of various salts and as a rule with the mixtures which are found in the rare earth minerals; the solubilities of a given salt of the various metals are not widely different. On this account separation by the crystallization of the nitrates or double nitrates is not rapid, while with the chromates accurate conditions must be observed, in which case this method gives splendid results.

The decomposition of the nitrates by heat is slow, but can, by patience, be carried out with success. The basic nitrate method of Welsbach[1] which can be applied to the yttrium group is a combination of this method and that of fractional precipitation. It is more rapid and successful than either method alone.

The successful use of any of the methods for separating the metals of the yttrium group depends largely on the ratios of the various constituents present in the mixtures, as well as on the character of the elements to be separated. We note, for example, that Dennis and Dales[2] in their study of the yttrium earths from sipylite find that magnesia, as a precipitating agent, causes little change in the atomic weights and absorption spectra, while James[3] was more successful in using this method

[1] Monatshefte, 5, 508.
[2] THIS JOURNAL, 24, 428.
[3] *Ibid.*, 29, 495.

on gadolinite earths. James used the nitrate solution while Dennis and Dales used a chloride solution. The author in working in a nitrate solution with yttrium earths from monazite has found that various fractions acted quite differently toward magnesia, some showed marked differences in atomic weight and absorption spectra after treatment with magnesia, while others showed little change. It has been observed, moreover, that in order to work this method with any appreciable degree of success the magnesia must be freshly ignited. The various degrees of success with different methods can also be illustrated by the Welsbach method[1] of crystallizing the oxalates from an ammoniacal solution or by the James method[2] in which the "oxalate-carbonates" are crystallized from an ammonium carbonate solution of the oxalates. This method with gadolinite earths in the hands of James yielded first yttrium and successively fractions with higher atomic weight to ytterbium. In the author's hands, it has worked similarly with the yttrium earths from samarskite but on applying the same method to certain oxalates from monazite, atomic weight determinations showed that the elements with heavier atomic weight appeared first while the more soluble portion yielded fractions whose atomic weight was far below the more insoluble portions. In other words, we here have the same method producing opposite results with different mixtures of earths.

From time to time, it has been proposed to use salts of organic acids. The oxalates can be crystallized from either ammoniacal or ammonium carbonate solution, yielding a fairly rapid method of fractionation, or the oxalates can be crystallized from nitric acid solution yielding fractions of different atomic weights. The ethyl sulphates and the acetyl acetonates have been used by Urbain and others as means of separation in this group. The formates have been repeatedly used for fractionations. Salts of a number of organic acids have been prepared, but little has been done in the application of the derivatives as means of separation. Such salts as the tartrates, citrates and succinates have been prepared, but little has been attempted in the way of separation.

The tartrates and citrates of the yttrium earths appear as white gelatinous precipitates when a neutral salt of potassium, sodium or ammonium is added to a solution of the yttrium salt. In a similar manner, insoluble derivatives are formed with neutral salts of fumaric, maleic, tartronic, malic and malonic acids. The neutral succinates of the alkalis or ammonium deport themselves in a very interesting manner with the neutral nitrates of the yttrium earths.

When neutral ammonium or sodium succinate is added to a neutral nitrate solution of the yttrium earths and the solution allowed to stand,

[1] Monatshefte, 27, 935.

[2] This Journal, 29, 495.

a finely divided crystalline precipitate of the succinates appears. This insoluble precipitate forms slowly, in fact, in the cold a few hours are necessary to insure complete precipitation. On the other hand, when the solution is hot or boiling, complete precipitation is effected in much less time, from ten minutes to half an hour being sufficient time for complete formation of the insoluble succinates. The ready formation of this finely divided precipitate and the fact that the reaction is far from instantaneous appears to us as promising to be a satisfactory method for fractionation. The fact that it forms as slowly as it does, would indicate that there should be plenty of time for equilibrium to be established and the physical character of the salt and its insolubility enables it to be quickly filtered and readily washed.

That the yttrium earths form succinates was shown by Berlin in 1835.[1] He showed that with sodium succinate the yttrium earths form a fine crystalline powder. Ekeberg in 1802[2] thought that the yttrium earths were not precipitated by the alkaline succinates while beryllium was, which was contrary to the results found by Berlin and to the work of Cleve and Höglund[3] who showed that ammonium succinate precipitates yttrium but not erbium from nitrate solution, but out of a mixture precipitates both.

In the thorium cerium group, Berzelius showed in 1829[4] the formation of an insoluble succinate of thorium. This reaction has been later studied by Kaufmann[5] and Schilling.[6] The use of an alkaline succinate has been recommended as a means of separation of iron from the gadolinite earths by Gadolin, Vauquelin, Berzelius, Berlin, and Hermann, after Klaproth had shown that iron would be first precipitated from such a solution.

The yttrium earths from samarskite have been studied with the view of testing the applicability of the succinates as a means of separation in this group.

Treatment of Samarskite.

Fifteen pounds of samarskite, containing very little gangue minerals were treated with concentrated hydrofluoric acid according to the method of J. Lawrence Smith. The mineral dissolved with effervescence. The columbium and tantalum passed into solution while the earths appeared as insoluble fluorides. These insoluble fluorides were thoroughly washed with water by decantation, after which they were dried and treated with concentrated sulphuric acid. After the first copious evolution of

[1] Pogg. Ann., 43, 108.
[2] Gilb. Ann., 14, 247; Ann. chim. phys., 43, 228.
[3] Ber., 6, 1468.
[4] Pogg. Ann., 16, 385.
[5] Dissertation Univ. Rostock, 1899.
[6] Dissertation Univ. Heidelberg, p. 141, 1902.

hydrofluoric acid, the mass was warmed and finally heated until the heavy fumes of the sulphuric acid came off. The pasty mass was allowed to cool; when it was extracted with water and the insoluble residue, which consisted of more or less of the oxides of columbium and tantalum, insoluble sulphates and a little undecomposed mineral was thoroughly washed with water by decantation. This sulphate solution of the earths and uranium was nearly neutralized with sodium hydroxide. Oxalic acid was then added, and the oxalates precipitated. These crude oxalates were ignited to oxides, dissolved in nitric acid, and treated with a hot saturated solution of potassium sulphate, with the addition of the solid salt. The soluble yttrium double sulphate solution was precipitated with oxalic acid, the oxalates were roasted to oxides, from the nitric acid solution of which it was again treated with potassium sulphate. Three such treatments with potassium sulphate from the nitrate solution were found necessary to completely remove the more insoluble group of earths and after three such treatments the didymiums could not be detected in a strong solution of the nitrates by means of their characteristic absorption spectra nor could cerium be detected by means of hydrogen peroxide.

Fractionation of the Succinates.

WITH R. C. BENNER.

About one hundred grams of the oxides were dissolved in nitric acid and the slight excess of free acid neutralized in ammonia. This neutral nitrate solution was diluted to a liter, brought to boiling and a saturated solution of neutral sodium succinate added in portions of 100 cc. By this means twelve fractions were obtained. After the addition of each portion of the sodium succinate, the solution was boiled fifteen minutes, after which the succinates were filtered and washed with 400 cc. of hot water. The fractions thus obtained were dried and ignited to oxide, small portions being taken for the determination of the atomic weight and the study of the absorption spectra.

SERIES I.

	Weight of fraction as oxide. Grams.	Atomic weight in R_2O_3.
1	22.2	114.2
2	15.8	111.83
3	10.0	110.06
4	8.8	111.30
5	9.0	108.5
6	7.1	107.2
7	7.0	105.6
8	6.1	104.4
9	7.0	101.0
10	6.4	97.0
11	4.0	95.8
12	3.0	....

The fractions thus obtained were combined and refractionated, selection being made of the portions whose atomic weights were close to each other; thus, for the second series, 2, 3 and 4 were combined and 5, 6, 7 and 8 were united while the lightest material, 9, 10 and 11, was similarly combined.

These oxides were dissolved in nitric acid, the excess of nitric acid removed by evaporation and in a dilution similar to that in Series I were fractionated by addition of sodium succinate in fractions as before. By again combining fractions of close atomic weight in three such series of fractionations the most soluble succinate fraction gave a nearly white oxide, whose nitrate solution showed only very weak absorption bands. The atomic weight of the element in the most soluble portion was 93, and the fraction corresponds to yttrium containing small amounts of samarium, europium and holmium as shown by the absorption spectra.

On the other hand, the third fraction at the other end of the series or the most insoluble portion gave a yellow earth whose atomic weight corresponded to 139. This oxide dissolved in nitric acid to a pink solution and showed absorption bands and was doubtless a mixture of yttrium with terbium, holmium, europium, samarium and erbium. Further study of these earths is being continued.

It has been considered well worth the while in making these studies on the samarskite earths and on the work which is in progress on the yttrium earths from monazite to determine the atomic weight in each fraction and also to study the absorption spectra.

The determination of the atomic weight for control purposes can be carried out sufficiently accurately by the estimation of the oxalic acid and of the earth oxide in the oxalate. While it is true that this method has some serious defects yet very good results can be obtained if it is properly handled.

Baxter[1] has recently shown in splendid detail that when the oxalates of neodymium, praseodymium, yttrium and certain other of the rare earths are precipitated in neutral or nearly neutral solution, they exhibit a strong tendency to carry down ammonium oxalate. This carrying down of ammonium oxalate by the insoluble oxalates of the yttrium earths is very pronounced and is difficult to prevent without going to the opposite extreme and making the solution too acid, in which case we have the factor of the solubility of the oxalate in acid appearing and the obviously incomplete precipitation of the oxalate. In the first case, the result due to the presence of additional oxalic acid in the precipitated oxalate would cause the atomic weight to be too low, while if considerable free nitric acid is present, the more soluble yttrium oxalate in incompletely precipitated and the result is to obtain a high atomic

[1] THIS JOURNAL, 28, 1684.

weight, due to the greater solubility of yttrium oxalate in nitric acid than of those earths of higher atomic weight.

The most accurate method for the precipitation of the oxalate of the yttrium earths which has come to the attention of the author has been to use a gram or less of the nitrate in very slightly acid solution and to use a dilution of about 500 cc. The oxalate is precipitated from the boiling solution by means of a dilute solution of pure oxalic acid.

In conclusion, the author wishes to acknowledge his appreciation of the courtesy of Mr. H. S. Miner, of the Welsbach Co., of Gloucester, N. J., who has placed at our disposal a large quantity of rare earth residues from Carolinian monazite and who has been able to secure for us a quantity of rare minerals for the study of the chemistry of the metals of the yttrium group.

UNIVERSITY OF WISCONSIN,
MADISON, WIS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

MODIFIED SPECTROSCOPIC APPARATUS.

BY GREGORY PAUL BAXTER.

Received January 22, 1908.

In examination of absorption spectra of dilute solutions in long tubes, the faintness of the spectra owing to the necessarily great distance of the source of light from the slit is frequently a disadvantage. A form of container which partially obviates the difficulty is easily constructed of the shape shown in Fig. 1 from a T of glass tubing of suitable diameter. The light passes through the tube B lengthwise and is focused upon the slit S by the solution in the tube A, which acts as a cylindrical lens, thus very much increasing the light intensity. If the tube B is long, the length of path of the outside and middle rays of the beam within the tube is essentially the same, so that absorption is nearly equal in all parts of the beam. Hence this form of apparatus does not possess the disadvantage of a simple cylindrical vessel in which the outside rays pass through a relatively shorter length of solution.

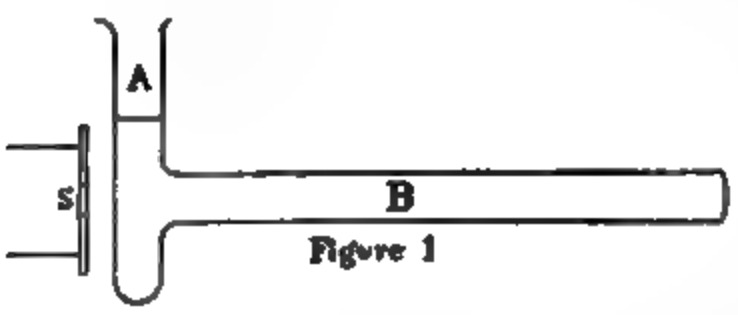


Figure 1

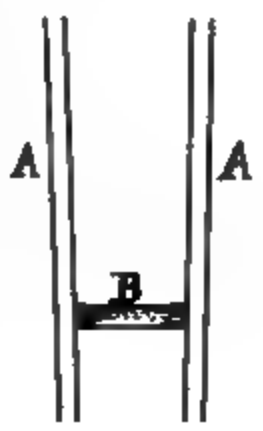


Figure 2

Fig. 2 illustrates a very convenient form of fulgurator for the examination of the spark spectra of a number of different solutions at one time. Such a process is frequently much retarded by the inconvenience in cleaning the ordinary forms of fulgurating apparatus between the examination of each two solutions. Two glass tubes, AA, into one end of each of which platinum wires have been sealed, are fused together in a nearly parallel position by means of a short piece of glass rod, B. One of the wires is bent in the form of a U so that the end is directly below and parallel to the wire in the other tube. The end of the lower wire may be covered with a glass capillary, C, in the usual way. The apparatus is dipped into the solution to be examined until the capillary is completely filled with solution. This system can be readily transferred from one vessel to another and can easily be rinsed into the vessel in which it has been used. If a rod is used in joining the tubes together the tubes may be brought so near without danger of short-circuiting that the apparatus is narrow enough to be inserted into a large sized test-tube. If the tubes are joined through a *tube* there is some difficulty from this source.

CAMBRIDGE, MASS.,
January 26, 1908.

[CONTRIBUTION FROM THE UNIVERSITY OF WASHINGTON.]

SIMPLE DEMONSTRATIONS OF THE GAS LAWS.

BY WILLIAM M. DEHN.

Received January 31, 1908.

The experiments usually given in textbooks to demonstrate Charles's law and Boyle's law involve pieces of apparatus so heavy or so complicated that they are unsafe or too time-consuming to be put into the hands of beginners in chemistry. That a knowledge of these laws and of the effect of aqueous vapor on gases should be developed early in chemical instruction can scarcely be denied, but almost no laboratory course for beginners gives time or attention to these demonstrations. If considered at all and apart from the study of physics, their demonstration is given in the chemical lecture and inevitably large numbers of students fail to develop a working knowledge of the individual laws or a rational conception of their joint application in the formula:

$$V = \frac{v(p - a)273}{760(273 + t)}. \qquad \text{(I)}$$

With the apparatus described below, involving use of the moving drop of mercury,[1] all of these effects of heat, pressure and aqueous vapor may not only be demonstrated and calculated *within one hour by the student*, but the pieces of apparatus represent small initial cost

[1] THIS JOURNAL, 29, 1052.

and minima of liability of breaking. Furthermore, these forms place in the hands of students instruments that not only admit of great accuracy but of direct *visible demonstration* of the laws. Finally these instruments not only avoid the necessity of making weighings but may in a simple manner demonstrate the *joint effect* of heat, pressure and aqueous vapor, as embodied in the above-written gas formula.

Charles's Law.—Part I consists of a calibrated bulb, A, and a graduated stem, B, whose internal diameter is less than 3 mm. Having been cleaned properly and filled with air, which must be dry or low in aqueous vapor, the mercury drop is adjusted to a position in the bulb end of the stem.[1] A rubber tube of convenient length is placed over the end of the stem and the apparatus, except the end of the rubber tube, is immersed in a pneumatic trough or a convenient form of water

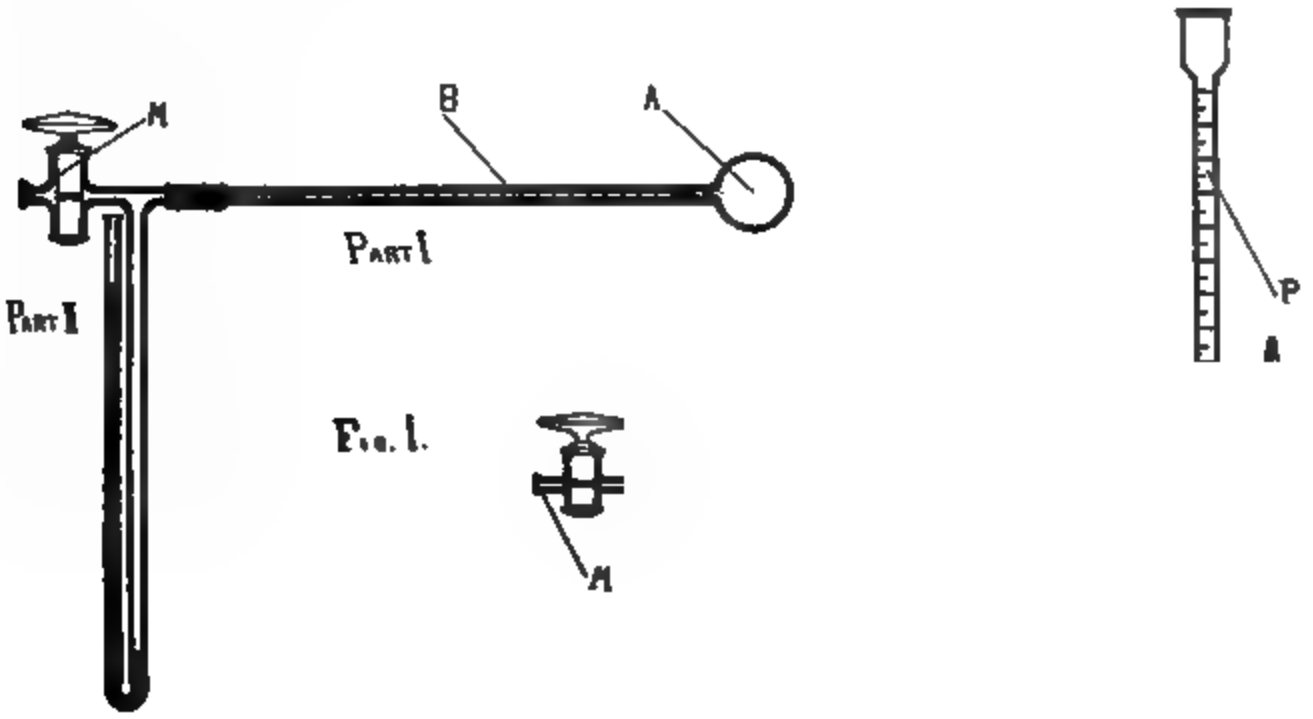


Fig. 1.

bath whose temperature is near that of the room.[2] After adjusting the mercury drop, the temperature (t) of the bath and the volume of the air confined in the apparatus (v) are read. Hot water is then poured

[1] Of course if changes of volume at lower temperatures are to be studied, the mercury drop is adjusted near the open end of the stem. However, when working at lowered temperatures, it should be remembered that the air contained in the apparatus must be dry.

[2] The most simple method for the student is to place the instrument and a thermometer flat on the bottom of a pneumatic trough and to fill up with the necessary quantity of tap water. For the second readings, a beaker of hot water is prepared and added to the tap water. Increases of 20–30° are usually sufficient.

into the bath and, after complete readjustment of the mercury-piston, the increased temperature (t') and the increased volume (v') are read. The mathematical relation,

$$v : v' :: (273 + t) : (273 + t'), \qquad \text{(II)}$$

is shown by the data to be correct or is approximated very closely.[1]

Boyle's Law.—For this experiment Part II (Fig. 1) is attached to Part I and the whole apparatus is suspended on the ring of an ordinary tripod. After adjusting the mercury drop near the rubber connection of Parts I and II,[2] the atmospheric pressure (p) and the volume of the contained air (v) are read. Air from the lungs is then blown into the instrument at the point M, the mercury rises in the manometer, as shown in the figure, while the mercury drop moves along toward the bulb end. The stopcock is then closed and the volume of the contained air (v'') is read and the height of the mercury column in the manometer is measured and added to the atmospheric pressure as the increased[3] pressure (p''). The mathematical relation,

$$v'' : v' :: p'' : p', \qquad \text{(III)}$$

is shown to be correct or is approximated very closely.[4]

Aqueous Vapor.—The instrument (Part III of Fig. 2) and the methods used to determine aqueous vapor are fully described in the previous contribution.[5] Since the *volume* occupied by the aqueous vapor in air is actually determined in this experiment, its relation to the atmospheric pressure as a *partial pressure* (a) is easily developed and the true pressure of a gas containing watery vapor is seen to be $p - a$.

Almost invariably students meet with difficulty both in embodying in the gas formula the above-derived mathematical statements of the laws but also in conceiving that they really are embodied in the formula. These difficulties may be removed (1) by constant practice in successive

[1] If the *absolute temperature* is to be calculated, x in the derived equation,

$$x = \frac{v't - vt'}{v - v'},$$

shows from the experimental data close approximation to 273. Of course, the *increment of volume* for 1° C, is equal to $1/x$ and should approximate $1/273$.

[2] Since it is more convenient to use separate instruments for the two experiments, no readjustment of the mercury drop need be made by the student. The proper initial adjustments may be made by the instructor and the same instrument may then be used by the students for series of duplicate experiments.

[3] When the mercury drop starts near the bulb end, air may be *drawn from* the apparatus and thus the effect of *reduced* pressure may be shown. In either case the height of the manometer needs to be only a little greater than 100 mm., since this is about the average pressure of air blown from or drawn into the lungs.

[4] The average error in a class of twenty freshmen was found to be only 0.1 per cent. or an error of one part in a thousand.

[5] THIS JOURNAL, 29, 1052–55.

application of the respective laws, (2) by development of the formula[1] from the above-derived mathematical statements of the laws, and (3) by experiments involving the simultaneous effects on gases of changed temperature, pressure and aqueous vapor pressure.

Joint Effects on Gas.—The apparatus depicted in Fig. 2 is employed to show the simultaneous effects on gas volumes of changes of temperature, pressure and aqueous vapor. When the aqueous vapor pressures (a and a') at different temperatures are taken from tables, the following method is employed: The instrument is filled with ordinary air and set up in the waterbath in the manner shown in the figure. A small measured quantity of water is run in; the volume occupied by the moist enclosed air (v), the temperature of the bath (t), the barometric pressure (p) and the aqueous pressure (a) are read. The water of the bath is gradually replaced by warmer water, until the mercury drop has moved to the limits of graduation on the manometer end of the scale; the mercury in the manometer indicates the resulting increased pressure. Should greater increased pressure be desired, sustained blowing at m produces another rise of mercury in the manometer and a simultaneous repulsion of the mercury drop along its scale. A further increase of temperature may now be made, provided the manometer can sustain an increase of pressure. The final volume (v'), temperature of the bath (t'), internal pressure (p') and aqueous pressure (a') are read. The data show that

$$\frac{v}{v'} = \frac{t(p' - a')}{t'(p - a)} \qquad \text{(IV)}$$

or that

$$v = \frac{v'(p' - a')\,t}{(p - a)t'}$$

from which, if the initial volume had been that of a dry gas at 0° C. and 760 mm., the usual gas formula may be derived.

[1] The following is given as an example of development of the gas formula. The effect on a gas of a change of temperature is shown in equation (II). Let v' be the volume at 0° C. (t') and any undetermined pressure. Solving, we have

$$v' = \frac{v(273 + t')}{273 + t} = \frac{v\,273}{273 + t}.$$

The effect on a gas of a change of pressure is shown in equation (III). Let v'' be the volume at 760 mm. (p'') and at 0° C., studies of changes of volume at different pressures may be made at this or any other temperature. Solving, we have

$$v' = \frac{v''p''}{p'} = \frac{v''760}{p'}.$$

Equating the values of v'', we have

$$\frac{v''760}{p'} = \frac{v\,273}{273 + t} \quad \text{or}$$

$$v'' = \frac{vp'273}{760\,(273+t)} = \frac{v(p - a)273}{760\,(273+t)}$$

in which $p - a$ is the true pressure exerted by the gas.

Should it be desired to determine experimentally all of the factors (*i. e.*, a and a') of the above equation (IV), the following method may be employed: The apparatus is first filled with dry air. After adjusting the mercury drop, the volume of the contained dry air, the temperature of the bath (t) and the barometric pressure (p) are read. A small measured quantity of water is then run in and the new volume (v) is read. From the data obtained, the aqueous pressure (a) is calculated. After v', p' and t' have been determined by the method described above, the water of the pipette (P) is replaced by concentrated sulphuric acid and a measured quantity of the acid is run in. After the internal pressure (p') is restored by blowing at M, the volume of contained dry air is read and the original aqueous vapor pressure (a') at p' and t' is calculated.

SEATTLE, WASHINGTON.

AN IMPROVED HYGROMETER FOR DETERMINING THE MINIMUM TEMPERATURE OF GAS IN DISTRIBUTION MAINS.

BY C. C. TUTWILER.

Received January 17, 1908.

In the distribution of illuminating gas, it has been found by repeated experiments that the gas will leave the works storage holder saturated with water vapor and also with the vapors of unfixed hydrocarbons, which latter contribute largely to the photogenic value of the gas. This condition of saturation is due to the fact that the gas reaches a temperature in the storage holder which is lower than any temperature to which it has been previously subjected up to this point, and it is therefore saturated with water and hydrocarbon vapors at the temperature of the holder. It has also been found that when the gas enters the relatively colder distribution mains some of these vapors will be dropped, the amount remaining saturating the gas at the lower temperature.

These vapors are unavoidably present. They are not vapors of the oil used in making the gas but are high temperature products of the closed ring series of hydrocarbons formed by the heat necessary to break up the oil into permanent gas. The manner in which these hydrocarbons are dropped out of the gas and again reabsorbed and the effect upon the candle power of the gas is an interesting study which need not be discussed at present, as it has only an indirect bearing upon the subject of this paper. It may not be out of place to say, however, that the aim of the gas engineer is to eliminate from the gas as many of the vapors of low tension high boiling hydrocarbons as possible and to retain those whose tension will permit of their being carried to the burner under all conditions of temperature and pressure met with during distribution.

It is evident that if the gas could be delivered to the consumer at a temperature equal to or greater than that obtaining in the storage holder, there would be no loss of light-producing hydrocarbons in the mains, and the candle power of the gas delivered at the burner, would be the same as that shown at the outlet of the storage holder. While this might seem to represent an ideal method of distribution, it is not practicable from an economic standpoint, as the temperature to which the gas is subsequently cooled in the mains during some seasons of the year is far below the outlet temperature of the storage holder and the cost of reducing the gas to the temperature of the mains at these times would more than offset any advantage gained. It has been found that the gas in the distribution system quickly reaches the temperature of the earth surrounding the mains, and where the mains are exposed, it may even be cooled to the surrounding atmospheric temperature. The attendant loss of hydrocarbon vapors and therefore loss in candle power is considerable, depending upon the so-called "permanency" of the gas and the degree of cold to which it has been subjected. Gases which owe a large percentage of their photogenic value to so-called unfixed hydrocarbon vapors will suffer a greater loss in this respect than those that contain a relatively greater amount of fixed hydrocarbons.

When, therefore, it is required to deliver to the consumer a gas of a uniform candle power throughout all seasons of the year, it is necessary to turn into the distribution mains a gas sufficiently high in candle power to take care of subsequent losses in the mains, which losses will vary from day to day.

The problem at once presents itself as how best to determine what this initial candle power should be, since any excess over and above that actually necessary, means financial loss to the gas company on account of extra enrichment or on the other hand may subject it to penalization if it should fall below that required by contract.

Since the loss in candle power is due to reduction in temperature of the gas in the mains, it will appear at once that the first thing to be determined in the above problem is the minimum temperature to which the gas will be cooled after it leaves the holders, and after having found this temperature to raise or lower the candle power of the holder gas to such an extent that when it is cooled down to the minimum temperature it will still have a candle power equal to that which must be furnished to the consumer.

It was found impossible to determine the minimum temperature by means of thermometers placed in the mains, as the gas continually changed in temperature, owing to its passage through more or less exposed portions of the mains, or on account of its being subjected to other conditions tending to change its temperature, such as rate of flow or nature

of the ground through which the main passed. For these reasons the location of the point of minimum temperature by means of thermometers was found to be exceedingly difficult and unreliable and the attempt was abandoned. A method was finally evolved which depended, for its successful operation, upon the following data:

In the course of a series of experiments made in the Philadelphia Gas Works, it was found that if a gas was cooled down in contact with its condensate to a lower temperature than any to which it had been previously subjected and then allowed to warm up in contact with its condensate to within a few degrees of the original temperature, or, to its original temperature out of contact with its condensate, the water which it would then contain as determined by means of calcium chloride, would just saturate it at the minimum temperature to which the gas had been cooled. An explanation of this is found in the fact that if oil and water are simultaneously deposited the oil will form a film upon the surface of the water, preventing its being again picked up when the temperature is raised so long as any oil remains. It appeared that advantage might be taken of this action and the minimum temperature which the gas had reached in the mains up to any given point be ascertained by determining its water dew point. For this purpose, an ordinary wet and dry bulb psychrometer was employed, the instrument being hung in a bell jar sealed in mercury, through which a current of the gas to be tested was continually passing. The dry bulb thermometer indicates the true temperature of the gas, while the wet bulb thermometer registers the temperature of evaporation, which is usually several degrees below the temperature of the gas. In saturated gaseous atmospheres, the thermometers will read alike and difference will be recorded in proportion to the dryness of the gas. The dew point may be obtained by means of these observations from Glaisher's table by multiplying the difference between the reading of the two thermometers by the factor opposite the dry-bulb reading and subtracting the product from the dry-bulb reading.

This instrument was given a thorough trial and though it furnished some very valuable data, its lack of portability and the knowledge that under the best conditions its indications were known to be only approximately near the truth, caused us to continue our efforts to devise a more satisfactory apparatus.

It was suggested at this time by Mr. Chas. O. Bond, chief photometrician of The United Gas Improvement Company, that the instrument devised by Regnault[1] known as the condenser hygrometer might be adapted to our needs.

The essential parts of this instrument comprise a thin-walled glass

[1] Ann. chim. phys. [3], 15, 129.

vessel quite similar in size and shape to an ordinary 15 cc. test tube, provided with a delicate thermometer and having means for passing air through a small amount of ether contained in the tube. Upon exposing the tube to an atmosphere containing water vapor and reducing the temperature of the tube by volatilizing the ether, moisture will finally be deposited on its outer wall. When this occurs the temperature is read on the thermometer, which reading is the temperature at which the atmosphere would be just saturated with the moisture contained therein, or in other words, its "dew point." The apparatus as designed by Regnault was intended to be used for the determination of the dew point of the atmosphere only, but its principles were successfully utilized in an apparatus which was found to be applicable to the determination of the dew point of any gas. This was accomplished by providing means for surrounding the vaporizing tube with the gas to be tested by the use of an outside jacket through which the gas was made to flow and providing scrubbers for the removal of hydrocarbon and water vapors, the use of which will be explained later on. In the first apparatus designed, air was forced through the ether by means of a rubber hand-pump, and it was found that at times when the dew point was very low, moisture would be deposited in the tube from the air and so cloud the ether that the deposit of dew on the outside of the tube could be seen only with great difficulty. This trouble was finally overcome by using a current of the gas being tested to volatilize the ether, and besides correcting the trouble, the cumbersome hand-pump was thus done away with. This and other improvements tending to compactness, resulted in the improved apparatus about to be described.

The construction and operation of the apparatus is as follows: The interior glass vessel (A) known as the condensing tube, the thermometer (T) and the small tube (B) reaching to the bottom of the condensing tube by means of which the ether is volatilized are quite similar to the essen-

tial parts of Regnault's apparatus, and if this portion of the apparatus is detached from the jacket by unscrewing the collar (C), it may be used in the same way as the Regnault apparatus for obtaining the dew point of the atmosphere. In order, however, to adapt it to our purpose, the glass jacket (D) was provided, through which a stream of the gas to be tested could be made to flow, surrounding the condensing tube in its passage to the burner. The course of the gas from the time it enters the inlet (I) until it issues at the burner (E) on top of the instrument, is as follows:

The cock (F) at the base of the instrument is so constructed that the gas upon reaching the same can be made to flow straightway into the jacket (D) or made to first pass through one or other of the two scrubbing vessels (G and H). In either course it finally passes into the jacket (D) and surrounds the condensing tube (A). It then passes through the hole (J) in the screw cap covering the jacket, and into the tube (B) which runs to the bottom of the condensing tube. The gas after leaving the condenser tube passes into the cap (K) and is finally burned at the burner (E). If a few cubic centimeters of ether or other volatile liquids, such as pentane, are placed in the condensing tube the gas bubbling through will rapidly volatilize it, thereby reducing the temperature of the tube and causing a deposition of dew upon its outer wall as soon as the point of saturation is reached. As soon as this occurs, the thermometer is read and the dew point thus ascertained. It is obvious that the instrument may be placed on any convenient gas bracket and that a few moments will suffice for determining the minimum temperature to which the gas has been cooled, up to that point.

It has been found that the determinations made with the instrument under all ordinary conditions are very reliable. Cases arise, however, when in order to get a correct indication of the minimum temperature, it is necessary to make use of a rubber scrubber to remove some of the hydrocarbon vapors prior to testing the gas and more rarely to use a calcium chloride drying tube to remove a portion of the water vapor. For example, if the gas after having been cooled to its minimum temperature in the mains should pass through a section of main which for some reason was warmer and any liquid hydrocarbon was present in the main at that point, the gas would saturate itself at the higher temperature with hydrocarbon vapor and therefore the instrument would show the dew point of the water vapor which would correctly indicate the minimum temperature. If, however, the gas is first passed through the scrubber (G) which contains finely divided rubber, the hydrocarbon vapors will be removed to such an extent that the amount remaining will not saturate the gas before the dew point corresponding to the water vapor is reached. Such conditions are rarely met with in the dis-

tribution mains. It is well, however, as a precautionary measure to take both hydrocarbon and water vapor dew points and if the hydrocarbon vapor dew point is found to be higher than the water vapor dew point, the latter should be taken as representing the minimum temperature.

Again, it is possible that the gas after having reached its minimum temperature may warm up in contact with water vapor which has been introduced into the gas, as for example in purifiers where steam is admitted for manufacturing reasons. Under such conditions the calcium chloride scrubber (H) must be used and the dew point of the hydrocarbon vapors taken as the minimum temperature.

It is a very simple matter to test the gas in all three ways, *i. e.*, direct, through the rubber scrubber, and through the calcium chloride scrubber, and it has been found advisable in order to get a correct idea of what is taking place or what has taken place in the mains to frequently check the direct readings with readings made after scrubbing the gas.

Such observations also enable the gas engineer to judge whether the gas is being scrubbed by tar or heavy drips deposited in the mains or whether it is picking up hydrocarbons from the mains. If the gas has been cooled to a low temperature as it might be in passing through an exposed main as under a bridge and afterwards warmed up in the ground, as previously stated, we would expect the hydrocarbon vapor dew point to be higher than the water vapor dew point. If the hydrocarbon vapor dew point is lower than the water vapor dew point, it would indicate contact of the gas with a deposit of tar or heavy drip oil.

The practical application of this instrument in gas distribution practice is well defined. Owing to its low specific heat, the gas flowing from the works quickly reaches the temperature of the surrounding earth. The gas engineer knowing by this instrument to what extent the hydrocarbon vapors have been dropped and what the consequent fall in candle power will be, is capable of anticipating the reduction in candle power by raising the candle power of the gas going into the holder accordingly.

LABORATORY OF THE
UNITED GAS IMPROVEMENT COMPANY, PHILADELPHIA,
December 18, 1907.

TECHNICAL METHOD FOR THE DETERMINATION OF LEAD IN ORES, ETC.

BY A. H. LOW.

Received January 28, 1908.

The following scheme is the result of many attempts on my part to improve the methods wherein lead is separated as oxalate and subsequently titrated with permanganate. I have used the method as described below for several months and have found it more satisfactory

for technical work than any other with which I am acquainted. Duplicate assays usually check within one-tenth of one per cent. A test of five portions of pure lead, weighed so as to approximately represent 3, 12, 20, 45 and 60 per cent. of lead in an ore, and put through the entire process, showed errors of —0.01, —0.06, +0.01, +0.05 and +0.05 per cent., respectively, the average error being 0.036 per cent. The permanganate was standardized on about 0.200 gram of lead.

Chromate-Oxalate Method.—Take 0.5 gram of ore and treat in a 6-oz. flask by the usual methods to obtain the washed lead sulphate, etc., on a 9 cm. filter. Dissolve the lead sulphate on the filter by stirring it up repeatedly with a jet of hot sodium acetate solution contained in a wash-bottle, receiving the filtrate in the original flask. Prepare the solvent by diluting a cold saturated solution of commercial sodium acetate with an equal bulk of water and adding 40 cc. of 80 per cent. glacial acetic acid per liter. To test if the extraction of the lead sulphate is complete, the flask may be replaced by a small beaker, the washing continued and a little potassium dichromate added to the filtrate. If any lead chromate is produced, the mixture may be added to the clear solution in the flask. Agitate the extract in the flask and heat it if necessary to redissolve any separated precipitate. Add 10 cc. of a 5 per cent. solution of commercial potassium dichromate, heat to boiling and boil gently for a few minutes to render the precipitate basic and easily filtered. The change is shown by its becoming reddish yellow in color. Filter hot, wash out the flask with hot water and then wash the precipitate only once, simply to clean the upper edge of the filter. Place a wide-necked funnel in the flask, open the filter and spread it against the wall of the funnel and wash off the lead chromate with a jet of hot oxalic acid solution, using from 25 to 40 cc. Rinse down any adhering chromate in the flask with hot water. The oxalic acid solution consists of a cold saturated solution of commercial acid 1 part, water 3 parts. Heat nearly to boiling in a wash-bottle. To the mixture in the flask add grain alcohol and then boil until the chromic acid is all reduced and the lead converted to oxalate. Remove from the heat, add 30 cc. of cold water and cool thoroughly, best under the tap or in cold water. When cold, filter through an 11 cm. filter, wash out the flask thoroughly with cold water and then wash filter and precipitate 10 times with cold water. Place 5 cc. of strong sulphuric acid in the flask, dilute first with a little cold water and then with hot water to about 125 cc. Add the filter and precipitate and titrate to the usual pink tinge with standard potassium permanganate solution. The solution used for iron will serve, although too strong for the best work. Theoretically, the oxalic acid ($C_2O_4H_2.2H_2O$) value of the permanganate multiplied by 1.642 will give the lead value, but owing to slight losses as sulphate, oxalate, etc., and

the fact that the lead oxalate is not perfectly pure, the factor 1.669 will give a closer approximation. On this basis, for 0.5 gram of ore taken for assay, the solution should contain 1.5185 grams of potassium permanganate per liter, in order that 1 cc. may equal 1 per cent. lead. It is best to standardize on about 0.200 gram of pure lead dissolved in a little 1:2 nitric acid and put through the entire process.

Notes.—The lead oxalate formed in the above process is not pure white, but yellowish, and still contains about 1 per cent. of lead chromate. It appears to be sufficiently uniform in its nature to give accurate results.

Instead of dropping filter and precipitate into the flask for titration, as described above, a neater method of procedure is as follows: Place the flask under the funnel and pour through and over the filter about 75 cc. of hot dilute acid, containing 5 cc. of strong sulphuric acid, and then wash the filter and residue well with hot water, so that the final bulk of the filtrate will be about 125 cc. Titrate the hot liquid as before. This method takes a little longer and gives practically the same results as the simpler way, but it has the advantage of a permanent end-point, there being no organic matter present to slowly decolorize the pink tinge.

Calcium does not interfere with the method, nor does antimony. Bismuth in small amounts is without material influence. Ten per cent. of bismuth added to a mixture containing about 23 per cent. of lead raised the result 0.36 per cent., most of the bismuth being removed as sulphate and chromate.

DENVER, COLO.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 150.]

THE ELECTROLYTIC DETERMINATION OF BISMUTH.

BY F. J. METZGER AND H. T. BEANS.

Received January 29, 1908.

Much has been written about the determination of bismuth in the electrolytic way and many electrolytes have been proposed. Without attempting any detailed discussion of the numerous publications which have appeared on the subject, the difficulties with which one almost invariably has to contend may be briefly summed up as follows:

When a bismuth solution is electrolyzed there is deposited not only metallic bismuth on the cathode, but frequently there is a simultaneous deposition of peroxide on the anode and it has been suggested that both anode and cathode be weighed for each determination. Again, the deposited metal is nearly always black and spongy, and in cases where accurate results have been obtained it has been necessary to exercise the greatest care in washing and drying in order to prevent loss mechanic-

ally. A method which has been recommended especially for comparatively large quantities of bismuth is the amalgam method originally proposed by Vortman.[1] In this method a known quantity of mercury salt is added to the bath and the deposit of bismuth amalgam weighed. From this weight the bismuth is obtained by difference. The quantity of mercury recommended is four times that of the bismuth present.

The method described in this paper presents none of the difficulties encountered in previous methods; the metal is deposited in compact, adherent form and can be washed and dried without any possible chance of loss, nor is there ever any deposition of peroxide on the anode when the electrolysis is completed.

It has been found that by the addition of acetic acid to a bismuth nitrate solution precipitation by hydrolysis may be completely prevented, even though the solution be subsequently largely diluted. It is also possible to obtain this result by first eliminating all free nitric acid by the addition of sodium hydroxide to alkaline reaction and then redissolving the precipitated bismuth hydroxide by means of acetic acid, the whole operation being carried out in the cold. It has also been observed that the addition of boric acid to the bath has a decided effect on the character of the deposit and in addition it serves to bring about, readily, complete solution of bismuth hydroxide without the addition of very large quantities of acetic acid.

The apparatus employed is a slightly modified form of that originally proposed by Gooch and Medway,[2] using a rotating cathode. The platinum thimble employed as cathode was connected to the shaft by means of a rubber stopper wound with fine platinum wire for contact and had an available surface of forty square centimeters. In all cases it was driven at the rate of about seven hundred revolutions per minute.

As a basis for the experiments a bismuth solution was prepared by dissolving chemically pure bismuth nitrate in water containing 25 cc. conc. nitric acid per liter. The solution was then carefully standardized by gravimetric methods.

The method of procedure was in all cases as follows: To a known quantity of the standard solution phenolphthalein was added, then sodium hydroxide solution, drop by drop, to alkaline reaction. The precipitate formed was redissolved in acetic acid and then two grams of boric acid were introduced. The solution was diluted, heated to 70–80° and electrolyzed. The working conditions are shown in the following table:

[1] Ber., 24, 2749.
[2] Am. J. Sci. [4], 15, 320.

TABLE I.

Expt. No.	50 per cent. acetic acid. cc.	Boric acid. Grams.	Volume. cc.	ND^2_{40}.	Voltage.	Temperature.	Time. Hrs.	Bi taken.	Bi found.	Error.
1	20	2	250	0.2–0.15	2.1 –2.8	74°–79°	¾	0.03956	0.0391	—0.00046
2	20	2	250	0.2–0.175	1.9 –2.75	75°–79°	1¼	0.0989	0.0990	+0.0001
3	20	2	250	0.2–0.15	1.9 –2.8	72°–75°	1½	0.0989	0.0990	+0.0001
4	20	2	250	0.2–0.17	1.9 –2.75	63°–77°	1¼	0.0989	0.0989	±0.0000
5	20	none	250	0.2–0.15	1.9 –2.7	74°–78°	1¼	0.0989	0.0989	±0.0000
6	20	2	250	0.2–0.15	1.9 –2.65	74°–83°	1¼	0.0989	0.0987	—0.0002
7	20	2	250	0.2–0.15	1.85–2.74	72°–77°	1¼	0.0989	0.0989	±0.0000
8	20	none	250	0.2–0.125	1.8 –2.6	77°–79°	1¼	0.0989	0.0986	—0.0003
9	20	2	250	0.2–0.2[1]	1.9 –2.8	75°–78°	1¼	0.0989	0.0984	—0.0005
10	20	2	250	0.2–0.17	1.85–2.75	76°–78°	1¼	0.0989	0.0992	+0.0003
11	20	2	250	0.2–0.17	1.8 –2.72	76°–79°	1¼	0.0989	0.0992	+0.0003
12	20	2	250	0.2–0.17	1.8 –2.64	77°–88°	1¼	0.0989	0.0991	+0.0002
13	20	none	250	0.2–0.175	1.8 –2.4	75°–78°	1¼	0.0989	0.0990	+0.0001
14	20	2	250	0.2–0.175	1.8 –2.7	73°–77°	1¼	0.1978	0.1981	+0.0003
15	20	2	250	0.2–0.16	1.8 –2.6	76°–77°	1¼	0.1978	0.1979	+0.0001
16	20	2	250	0.2–0.16	1.8 –2.55	73°–78°	1¼	0.1978	0.1978	±0.0000
17	20	2	250	0.2–0.17	1.77–2.55	70°–80°	1¼	0.1978	0.1980	+0.0002
18	20	none	250	0.2–0.175	1.75–2.37	75°–81°	1½	0.1978	0.1984	+0.0006
19	30	none	250	0.2–0.16	1.8 –2.45	70°–78°	2¼	0.3956	0.3962	+0.0006
20	30	2	250	0.2–0.175	1.75–2.5	70°–78°	2¼	0.3956	0.3953	—0.0003
21	30	none	250	0.2–0.15	1.7 –2.42	73°–79°	3¼	0.3956	0.3955	—0.0001
22	30	2	250	0.2–0.16	1.75–2.55	74°–77°	2¼	0.3956	0.3956	±0.0000
23	30	2	250	0.2–0.175	1.72–2.45	74°–79°	2¼	0.3956	0.3957	+0.0001
24	30	2	250	0.2–0.175	1.75–2.50	78°–79°	2½	0.3969	0.3968	—0.0001
25	30	none	250	0.2–0.175	1.76–2.55	75°–80°	3½	0.3969	0.3969	±0.0000

In Experiments 19–25 inclusive, the amount of acetic acid given does not completely redissolve the precipitate, but after the addition of the boric acid the solution becomes perfectly clear. In Experiments 19, 21 and 25, in which no boric acid was used, the slightly opalescent solution was electrolyzed, the solution, however, becoming perfectly clear during the period of the electrolysis.

The change in voltage during the electrolysis serves as an excellent indicator in the determination. The voltage remains constant until all but the last trace of bismuth has been deposited, when it begins to rise rapidly to a maximum at which it again remains constant. The electrolysis should be continued five or ten minutes beyond this maximum point. In the table given above the voltages recorded show the initial and final values. Table II being a record of Experiment 16 above, makes this a little more clear.

[1] In this experiment the current was maintained constant.

[2] The figures in the second column represent the point to which the current drops at the end of the experiment.

TABLE II.

Time. P. M.	ND_{40}.	Voltage.	Temperature.
2:50	0.2	1.8	73°
3:05	0.2	1.8	75°
3:20	0.2	1.8	76°
3:35	0.2	1.8	78°
3:43	0.19	2.0	78°
3:45	0.18	2.1	78°
3:50	0.175	2.4	78°
3:55	0.175	2.5	78°
4:00	0.160	2.55	78°
4:05	0.160	2.55	78°

The action of acetic acid on the deposited metal was found to be so slow that it is not necessary to siphon off the liquid at the end of the experiment. All that is required is to quickly substitute a beaker of water without interrupting either the current or rotator. The thimble is then detached, washed with alcohol and ether, allowed to dry and weighed after standing on the balance for ten minutes. To avoid any errors which might arise from changes in atmospheric conditions, the weight of the thimble was taken after dissolving off the deposited metal by immersing in nitric acid, washing and drying, etc., the same as above.

In all of the experiments given in Table I, the available cathode surface was forty square centimeters, and it was naturally supposed that a stronger current could be employed with a larger electrode, and in this way the time factor might be reduced. A large electrode having an available surface of one hundred square centimeters of the same form as the one previously used was procured with which we obtained the following result:

Expt. No.	50 per cent. acetic acid. cc.	Boric acid. Grams.	Volume. cc.	ND_{100}.	Voltage.	Temperature.	Time. Hrs.	Bi taken.	Bi found.	Error.
26	30	2	350	0.5–0.17	1.9–2.5	78°–80°	1½	0.3969	0.3972	+0.0003

In working with this larger electrode the current should be reduced to 0.2 ampere at the time when the voltage begins to rise.

As seen in the table the results are accurate without the use of boric acid. The metal is deposited in bright, compact form up to the time when the voltage begins to rise, *i. e.*, when only very small quantities remain in solution. From this point, if there be no boric acid present, the last traces of metal deposit over the surface of the bright coating in the form of a granular layer less firmly adherent and somewhat darker. With boric acid present the deposition is uniform to the very end of the experiment, giving a smooth, compact, adherent deposit having the characteristic color of the metal.

In not a single experiment was there any evidence of peroxide formation on the anode at the close of the determination. Occasionally there was a slight tinge of yellow on the anode at the very beginning of the electrolysis, but this, however, soon disappeared. The solution after each determination was examined for bismuth and none could be found.

The effect of boric acid on the deposition of other metals is being studied.

ANALYTICAL LABORATORIES,
January, 1908.

A SEPARATION OF IRON FROM MANGANESE.

BY RICHARD B. MOORE AND IVY MILLER.

Received December 30, 1907.

If to a solution of ferric chloride containing free hydrochloric acid, pyridine, in slight excess, be added, the iron is completely precipitated as hydroxide. Aluminium, chromium, and zinc, under such conditions, are not completely precipitated, while manganese, nickel, and cobalt remain in solution. This method can therefore be used to separate iron from the last three metals. The present paper deals only with the separation of manganese from iron by means of pyridine.

When pyridine is added to a neutral solution of a manganous salt no precipitate is obtained. On warming, the solution slowly oxidizes and the manganese begins to come down. The rate at which oxidation takes place, however, is about one-third as fast as the rate at which a manganous solution oxidizes when treated with ammonium chloride and ammonium hydroxide under similar conditions. If the manganous solution is made acid with a little hydrochloric acid before addition of the pyridine to slight excess, the solution may then be heated for ten minutes without oxidation. Consequently, pyridine possesses considerable advantages over ammonium hydroxide in the separation under question, especially when a large amount of manganese is present. Practically, its only disadvantage is its cost. A very fair separation can be made with one precipitation.

On washing ferric hydroxide precipitated by pyridine, no iron at first appears in the filtrate. As the excess of pyridine is washed out of the precipitate, however, colloidal iron passes through the filter. On washing the precipitate with pyridine water (1:500) the iron is completely retained by the filter.

In the following experiments Merck's pyridine, "Medicinal grade," was used. It was redistilled before using.

Pure iron wire was dissolved in 10 cc. of 4 *N* hydrochloric acid. A few drops of concentrated nitric acid were added and the solution

warmed to oxidize the iron. It was then diluted to 100 cc., warmed, and pyridine added from a burette. The precipitate was washed with pyridine water (1:500):

	Iron taken. Gram.	Iron found. Gram.
No. 1	0.0806	0.0807
" 2	0.0823	0.0824
" 3	0.0798	0.0810

In No. 1, the pyridine was added until the iron was just precipitated. In No. 2 there was an excess of 0.5 cc. of pyridine, and in No. 3 an excess of 1 cc.

Solutions of manganous chloride were then mixed in different proportions with ferric chloride. The amount of free acid was the same as was taken above. The precipitation takes place equally well in the cold or after gently warming. In the following series the manganese in the filtrate was not estimated, the object being to see what kind of a separation was made by a single precipitation. One-half a cubic centimeter in excess of pyridine was used in each case:

	Iron taken. Gram.	Iron found. Gram.	Manganese present. Gram.
No. 1	0.0797	0.0798	0.1405
" 2	0.0790	0.0792	0.0857
" 3	0.0791	0.0792	0.0719
" 4	0.0798	0.0802	0.0610

In the next series both the iron and manganese were estimated in order to see what effect the presence of the pyridine has on the precipitation of the manganese. The manganese cannot be completely precipitated by addition of bromine water to the hot solution. In addition, the formation of pyridine bromide interferes. In No. 1 the manganese was estimated in the usual manner by potassium carbonate. In numbers 2, 3 and 4, *c. p.* sodium hydroxide was used instead of the carbonate, the precipitation being made in porcelain basins:

	Iron.		Manganese.	
	Taken. Gram.	Found. Gram.	Taken. Gram.	Found. Gram.
No. 1	0.0858	0.0862	0.0698	0.0691
" 2	0.1136	0.1133	0.0667	0.0666
" 3	0.1162	0.1155	0.2289	0.2285
" 4	0.1268	0.1264	0.1145	0.1140

The conditions under which aluminum can be separated from manganese and aluminum and iron from beryllium by means of pyridine are under investigation.

CHEMICAL LABORATORY,
BUTLER COLLEGE, INDIANAPOLIS.

THE ACTION OF SODIUM BENZYL CYANIDE WITH CINNAMIC ESTER.

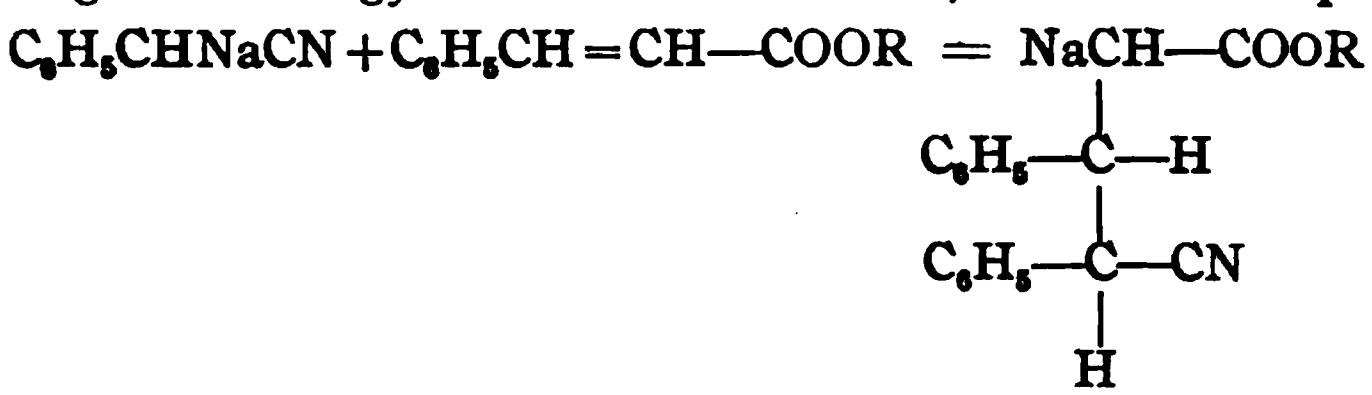
By S. Avery and G. R. McDole.

Received January 29, 1908.

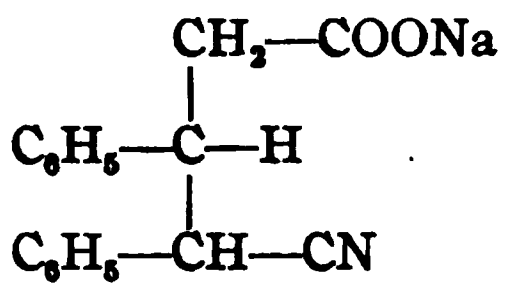
Introduction.

Victor Meyer and his pupils[1] have studied the character of the methylene hydrogen atoms in benzyl cyanide. They found, in brief, that these atoms resembled in some respects the corresponding atoms in acetoacetic ester and in malonic ester. The reactions studied related in general to the condensation with aldehydes, and to the substitution of alkyl radicles. Later Zelinsky and Feldmann[2] condensed benzyl cyanide and methylene iodide, forming the nitrile of symmetrical diphenylglutaric acid. Michael[3] has shown that sodium acetoacetic ester, as also sodium malonic ester, forms addition products with esters of the unsaturated acids. This reaction has been used by Auwers,[4] Perkins,[5] Avery,[6] and others in preparing alkyl glutaric acids. Having had occasion to try to effect the synthesis of certain alkyl glutaric acids the writers decided to study the action of benzyl cyanide on cinnamic ester. It was assumed that an addition product would be formed, which on saponification and the splitting off of carbon dioxide would give a diphenylglutaric acid. The results obtained have shown that the reactions which took place were not strictly analogous to Michael's as the following comparison shows.

Following the analogy of Michael's reaction, we should expect:

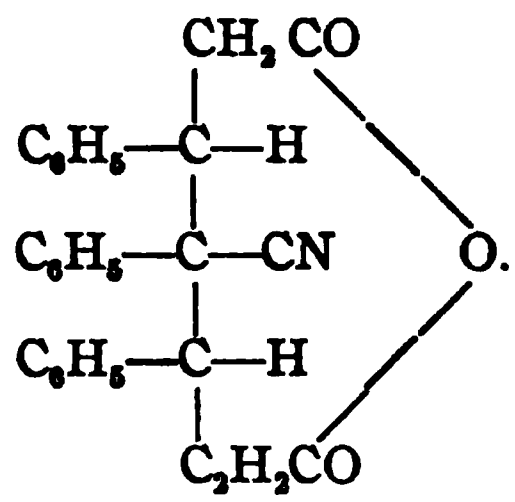


In reality, however, the reaction was accompanied by the saponification of the ester and the two principal products formed were



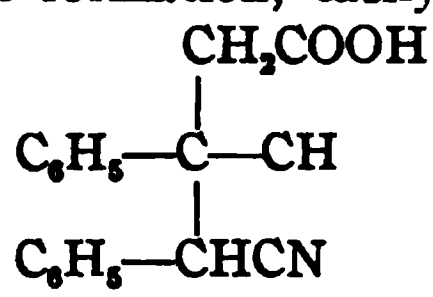
and a product to which we will provisionally ascribe the formula

[1] Ber., 20, 534; *Ibid.*, 21, 1291; Ann., 250, 118.
[2] Ber., 22, 3290.
[3] J. pr. Chem. [2], 35, 352.
[4] Ber., 24, 1936.
[5] J. Chem. Soc. (London), 69, 1472.
[6] Am. Chem. J., 20, 509; *Ibid.*, 28, 48.



This formula is in harmony with all of the facts observed except the following: It appears to be unchanged by boiling with sodium carbonate or ammonia, either in aqueous or alcoholic solution. Although it is converted into a salt by boiling with alcoholic potassium or sodium hydroxide, the acid liberated from the salt has resisted all attempts to reconvert it into an anhydride.

Of special interest is the formation, easily and in good quantity, of the compound:



This on reduction may be expected to yield β,γ-diphenyl-δ-aminovaleric acid, which on heating should form the corresponding piperidone derivative. This reduction will occupy our attention in the near future.

Experimental.

β,γ-Diphenyl-γ-Cyanbutyric Acid.—Twenty grams of benzyl cyanide were mixed with 30 grams of cinnamic ester, and solid sodium methylate equal to 4 grams of sodium was added with stirring. The mixture became hot and the action was apparently completed in a few minutes. When the action had ceased the product was allowed to stand on the waterbath for two hours. It now appeared as a viscous semi-crystalline yellow mass. On adding hydrochloric acid and stirring, it changed to a very viscous oily mass which on thoroughly acidifying and washing out the sodium chloride, gradually assumed a semi-crystalline condition. This was dissolved in hot benzene and on cooling hair-like needles separated out. On filtering off the mother liquor and condensing, a second crop of crystals was obtained. With careful manipulation the yield amounted to nearly 80 per cent. Almost equally good results were obtained when solid sodium hydroxide was used instead of sodium methylate.

During the reaction the escape of alcohol vapors was noticed.

The acid obtained was recrystallized from benzene. It melts at 161.5°, is easily soluble in alcohol, ether and hot benzene, difficultly soluble in hot and almost insoluble in cold water. Glistening white needles from benzene or dilute alcohol.

The analysis gave:	C, 76.67	H, 5.84	N, 5.19
Calculated for $C_{17}H_{15}O_2N$:	C, 76.98	H, 5.66	N, 5.28

Titration, 0.2101 gram required 7.55 cc. N/10 sodium hydroxide. Theory for one acid H in $C_{17}H_{15}O_2N$ requires 7.52 cc.

The silver salt is a white insoluble powder, which gave 29.01 per cent. Ag. Calculated, 29.03 per cent.

α,β-Diphenylglutaric Acid.—This acid was first prepared by us by adding sodium (1 atom) dissolved in ethyl alcohol to benzyl cyanide (1 molecule). After the action had ceased a molecular quantity of cinnamic ester was added. The action proceeded with the liberation of considerable heat. The resulting mass was viscous and light brown in color. This was acidified with hydrochloric acid and the sodium chloride washed out. The mass resisted all attempts to recrystallize. Attempts were made to saponify with potassium hydroxide, in one instance the compound above mentioned, the half nitrile acid was obtained in a very impure state. As a whole the saponification with potassium hydroxide was unsatisfactory and a product free from nitrogen could not be obtained by this method. The viscous mass was sealed in a Carius tube with concentrated hydrochloric acid and heated for five hours to 150°. The mass was extracted with boiling water several times and the remaining mass reheated and the process repeated. The aqueous extractions were condensed and a crystalline product was obtained which showed, under the microscope, crystals having both cubical and needle-like shapes. Varying products were obtained which melted from 195° to 215°. By careful recrystallization out of 50 per cent. alcohol the pure diphenylglutaric acid was obtained which melted at 223–4°. The crystals are needles. By working over the mother liquors from these recrystallizations, crystals of a cubical appearance were isolated. It was impossible to get very satisfactory melting points of any of the lower melting products but by repeated recrystallizations a substance was obtained melting almost constantly at 205°. This compound resembled the diphenylglutaric so closely that it was for a time thought to be a stereoisomer. Analysis for carbon and hydrogen agreed very closely with that of the glutaric acid, melting at 223–4°, and it formed an anilic acid which, though it melted about 30° lower, corresponded very closely in other respects with that obtained from the glutaric. However, very careful work showed the presence of a small amount of nitrogen in the supposed isomeric glutaric acid (m. 205°) and when this compound was placed in the sealed tube with hydrochloric acid and heated, the compound obtained was in every case the diphenylglutaric acid, melting at 233–4° and free from nitrogen. The cyanide group was either saponified or converted into insoluble combinations.

The diphenylglutaric acid can be obtained in quantity and without

the formation of objectionable by-products by heating the β,γ-diphenyl-γ-cyanbutyric acid with concentrated hydrochloric acid in a sealed tube to 150° for three hours.

The analysis of α,β-diphenylglutaric acid obtained as first mentioned gave: C, 71.86; H, 5.33. Calculated for $C_{17}H_{16}O_4$: C, 71.79; H, 5.67.

Titration, 0.1142 gram of substance required 8.01 cc. N/10 NaOH. Theory for $C_{17}H_{16}O_4$, 8.03 cc. N/10 NaOH.

The silver salt gave 43.34 per cent Ag. Theory for $C_{17}H_{14}O_4Ag$, 43.35 per cent.

Analysis[1] of the diphenylglutaric acid obtained by the saponification of the β,γ-diphenyl-γ-cyanbutyric acid gave: C, 71.59; H, 5.69. Calculated for $C_{17}H_{16}O_4$: C, 71.69; H, 5.67.

Titration, 0.1084 gram of substance required 4.05 cc. N/10 NaOH. Calculated for two acid hydrogens in $C_{17}H_{16}O_4$, 3.99 cc. N/10 NaOH.

The Anhydride.—Attempts were made to prepare the anhydride both by heating the acid above its melting point and by treatment with acetyl chloride and acetic anhydride. In all cases a brown product resulted which resisted our attempts to obtain it in a crystalline form.

Anilic Acid.—The anilic acid was prepared by heating some of the glutaric acid with acetyl chloride and boiling off the excess of acetyl chloride. It was then treated with the calculated amount of aniline dissolved in alcohol. The anilic acid separates out of dilute alcohol in flat needle-like crystals having a beautiful mother of pearl luster when dry. Soluble in ether and alcohol. Purified by recrystallizing out of alcohol. Melting point, 230–2°.

Titration, 0.1537 gram of substance required 4.25 cc. N/10 NaOH. Theory for $C_{28}H_{21}ON_3$, 4.28 cc. N; 10 NaOH.

The nitrogen determination gave 4.16 per cent. N; calculated, 3.93 per cent.

Other Products formed by the Action of Sodium Benzyl Cyanide on Cinnamic Ester.—Dry sodium methylate representing 4 grams of sodium was mixed with 20 grams of benzyl cyanide and the mixture heated to 140°. This was now added to 30 grams of hot cinnamic ester and the heating continued with constant stirring at the above temperature for ten minutes. The mass was cooled, treated with strong hydrochloric acid, well washed with water and then boiled with 95 per cent. alcohol. Partial solution took place accompanied by the separation of white crystals, which increased on cooling the mixture. These were filtered off, washed with a little alcohol, then a small quantity of benzene, dried and boiled with sodium carbonate solution, again filtered and dried. Yield, 9 grams.

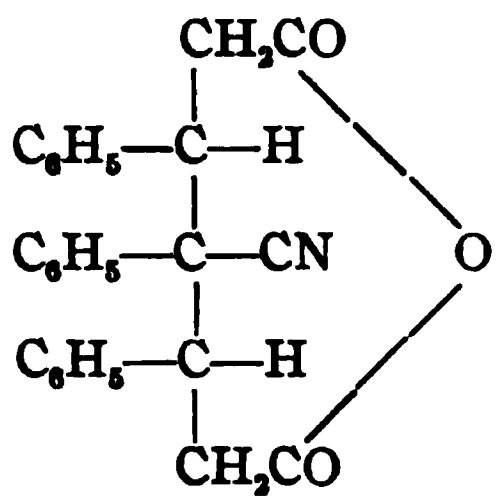
After having tried all of the ordinary solvents without satisfactory

[1] Analysis by C. J. Frankforter.

results, amyl alcohol was found to be well suited for the purpose of recrystallization. The pure compound forms long obliquely pointed plates, sometimes resembling needles, which melt at 231–3°. Insoluble in ammonia, sodium carbonate solution, and petroleum ether; difficultly soluble in alcohol, ether and benzene, soluble in hot acetic acid and amyl alcohol. It is unchanged by heating in a sealed tube with concentrated hydrochloric acid for 5 hours. It is, however, acted upon by a strong solution of alcoholic potash. The analysis corresponded to the formula $C_{26}H_{21}O_3N$. From all data at hand it corresponds to the anhydride of the acid resulting from the union of two molecules of cinnamic ester with one of benzylcyanide.

The following formula expresses this constitution but is put forth only tentatively:

The analysis gave:[1] C, 78.93; H, 5.59; N, 3.64. Calculated for $C_{26}H_{21}O_3N$: C, 79.04; H, 5.34; N, 3.55.



The molecular weight was determined by the freezing point method, using benzene as a solvent. The substance is so slightly soluble in this substance that the determinations were not very satisfactory. The mean of the two determinations gave 388 as the molecular weight. Calculated for $C_{26}H_{21}O_3N$, 396.

The Acid Obtained from the Supposed Anhydride.—When the compound last considered is heated for 10 minutes with very strong alcoholic potash it is dissolved and a sodium salt is obtained. This, upon acidifying, yields the corresponding acid. The acid was purified by dissolving in ether and evaporating the ether off in the presence of benzene. This was allowed to crystallize and recrystallized again out of 50 per cent. alcohol. The substance crystallizes in rectangular plates and under some conditions in crystals resembling cubes suggesting the impurity encountered with the α,β-diphenylglutaric acid. Soluble in ether and alcohol, sparingly soluble in benzene, and boiling water. Melts at 213°.

The analysis gave: C, 75.38; H, 5.56; N, 3.69. Calculated for $C_{26}H_{23}O_4N$: C, 75.54; H, 5.56; N, 3.39.

Titration, 0.2530 gram of substance required 12.05 cc. of N/10 NaOH. Theory for $C_{26}H_{23}O_4N$, 12.2 cc. N/10 NaOH.

[1] Analysis by C. J. Frankforter.

Silver salt is an insoluble white powder, darkening slightly upon exposure to light. It gave 34.40 per cent. Ag; calculated, 34.24 per cent.

We have attempted to saponify the cyanogen group of this compound and thus obtain the tricarboxylic acid but it has resisted all attempts. Neither potassium hydroxide nor hydrochloric acid in a sealed tube gave the desired result. We expect to investigate the character of this nitrogen atom and the salts of the acid more fully, as well as the exact constitution of the anhydride from which it was formed.

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THE SYNTHESIS OF CERTAIN AROMATIC SUCCINIC ACIDS.

BY S. AVERY AND FRED W. UPSON.

Received January 29, 1908.

In the preceding article by one of us and McDole it is pointed out that in the synthesis of α,β-diphenylglutaric acid apparently two stereoisomers were obtained. It was conceived, however, that one of these might be the isomeric succinic acid formed according to the reaction:

$$C_6H_5{-}CH{=}CHCOOR + C_6H_5{-}CHNa{-}CN = C_6H_5{-}CHNa{-}\underset{\underset{C_6H_5{-}CH{-}CN}{|}}{CH}{-}COOR$$

This ester on saponification would yield the unknown benzyl-phenylsuccinic acid.

For the purpose of comparing this acid with the product described in the preceding article it was decided to effect its synthesis in such a way as to leave no doubt in regard to its constitution.

Accordingly 25 grams of sodium benzylmalonic ester were condensed with 21 grams of bromphenylacetic ester. The heavy brown oily product thus obtained was heated in a bomb with hydrochloric acid but no crystalline product was obtained, although a large amount of carbon dioxide was liberated. The oil was then boiled with potassium hydroxide solution, in which it partially dissolved. On separating from the undissolved portion and acidifying, crystals mixed with an oil came down. This mixture was extracted several times with hot water, which on cooling deposited crystals in a fairly pure state. These were filtered off and washed free from oily and resinous matter with a mixture of chloroform and petroleum ether. After recrystallization from a mixture of ether and chloroform, pure white, very fine, needle-like crystals melting sharply at 176° were obtained. The acid is difficultly soluble in hot, almost insoluble in cold water; soluble in ether and alcohol; insoluble in chloroform and petroleum ether and difficultly soluble in benzene.

Titration.—0.0615 gram acid required 4.25 cc. N/10 sodium hydroxide; calculated for 2 acid hydrogens in $C_{17}H_{16}O_4$, 4.32 cc.

The silver salt is a white amorphous precipitate. It gave 43.13 per cent. Ag; calculated, 43.30 per cent.

The yield of the acid was very unsatisfactory and a considerable amount was lost in repeated recrystallizations to obtain an absolutely pure product from which to determine the melting point. As the analytical data above given indicated that the desired substance had been obtained, it seemed unnecessary to pursue the subject further, especially as in the meantime the nature of the apparently low melting glutaric acid had been determined.

While the work in this and the preceding article was in progress Higson and Thorpe[1] published an article describing the synthesis of alkyl succinic acids by the condensation of ethyl sodiumcyanoacetate with aldehyde cyanohydrines.

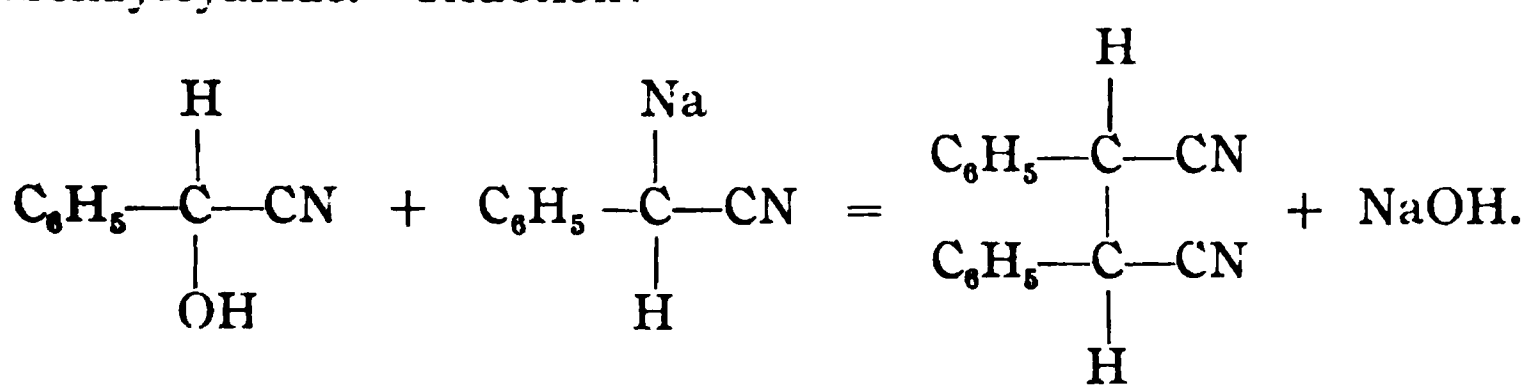
Quoting from their article: "The condensation between ethyl sodiocyanoacetate and either a ketone or an aldehyde-cyanohydrine proceeds in nearly all the cases investigated very smoothly at the ordinary temperature * * * * The reaction may be represented by the following general equation:

$$CHNa(CN).COOEt + HO{-}\underset{\underset{R}{|}}{C}.R.(CN) \longrightarrow CO_2Et.\underset{\underset{Na}{|}}{C}.(CN).\underset{\underset{R}{|}}{C}.(CN).R + H_2O.$$

* * * * The alkyl derivatives of succinic acid can then be prepared from these ethyl salts by hydrolysis with hydrochloric acid according to the equation:

$$CO_2Et.CH(CN).CR_2.(CN) \longrightarrow CO_2H.CH_2.CR_2.CO_2H''.$$

It seemed, therefore, of interest to see if benzyl cyanide could be made to condense in a like manner with aldehyde cyanohydrines in the synthesis of similar products. Accordingly, the first condensation attempted was between benzaldehyde cyanohydrine and sodiumbenzylcyanide which should give the nitrile of diphenylsuccinic acid. Thirty grams of benzaldehyde were treated with a saturated solution of acid sodium sulphite, and then with 29 grams of potassium cyanide, yielding 47.7 grams of the cyanohydrine. This was condensed with 49 grams of sodiumbenzylcyanide. Reaction:



The heavy black tarry mass resulting from the condensation was heated over the steam bath for several hours with a slight excess of sulphuric

[1] J. Chem. Soc., 89, 1455.

acid. On cooling, the mass became thick and showed the presence of crystals. These crystals, insoluble in benzene, were washed free from the oily, foreign substance with benzene, and then purified by recrystallization from glacial acetic acid. The first melting point on what appeared to be the pure substance was 188–190°. Several recrystallizations raised the melting point to 232°. It is recorded by Knoevenagel[1] that there are two isomeric modifications of this nitrile. One melts at 160° and may be changed to the other isomer melting at 239–240° C. After treating the compound in the manner described by Knoevenagel[2] the isomer melting at 239–240° was obtained.

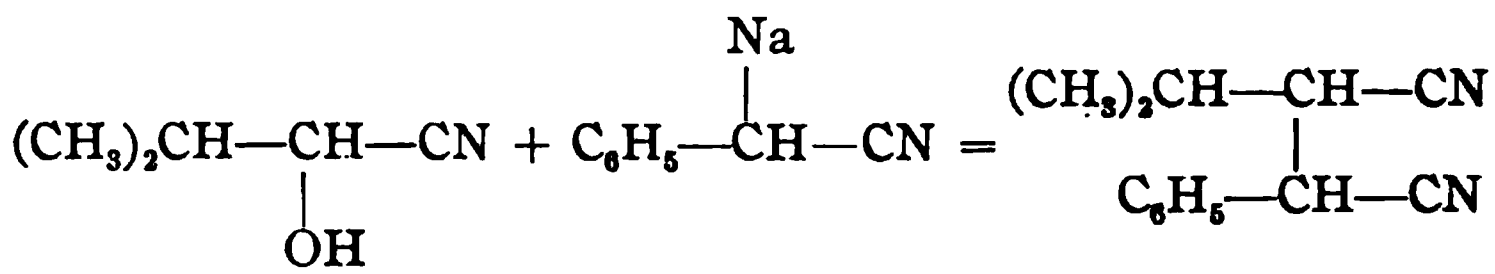
A nitrogen determination gave 12.28 per cent. N. Calculated for $C_{16}H_{12}N_2$, 12.09 per cent.

The nitrile was saponified by heating in a bomb for five hours with hydrochloric acid. The resulting crystals were purified out of alcohol and melted at 229°.

Titration.—0.10475 gram required 7.73 cc. N/10 sodium hydroxide; calculated for two acid hydrogens in $C_{16}H_{14}O_4$, 7.75 cc.

Since both the acid[3] and the nitrile[4] are known and are fully described in the literature, and since the analytical data given clearly indicate that the desired end has been reached, no further examination of this succinic acid was made.

In order to test this reaction, using an aldehyde of the aliphatic series, 25 grams of isobutyl aldehyde were converted to the cyanohydrine and condensed with sodiumbenzylcyanide. It was assumed that the nitrile of phenylisopropylsuccinic acid would be formed according to the equation:



The light brown oily condensation product was heated on the water bath for some time with a slight excess of sulphuric acid. On standing several days and with occasional stirring the mass showed evidences of forming crystals. When it had entirely solidified the crystals were purified by crystallization, first from alcohol and then from a mixture of petroleum ether and chloroform. White, feathery crystals, melting at 126°, were obtained.

A nitrogen determination gave 7.21 per cent. N. Calculated for $C_{13}H_{14}N_2$, 14.16 per cent.

[1] Ber., 25, 289.
[2] *Ibid.*, 25, 295.
[3] Ann., 258, 87; Ber., 14, 1802; Ber., 23, 117.
[4] *Ibid.*, 25, 289.

A titration at this point gave a similar result. 0.0856 gram required 3.82 cc. N/10 sodium hydroxide; calculated for one acid hydrogen in $C_{13}H_{15}O_2N$, 4.38 cc. N/10 sodium hydroxide.

These results seemed to indicate that the nitrile was partially saponified. Some of the nitrile was boiled with dilute sodium hydroxide and the crystals that came down on acidification were purified by crystallizing from a mixture of alcohol and a little petroleum ether.

Titration.—0.0756 gram required 3.45 cc. N/10 sodium hydroxide. Calculated for one acid H in $C_{13}H_{15}O_2N$, 3.48 cc.

Apparently one nitrile group had undergone saponification during the progress of the reaction. In this connection it may be noted that in the various cyanogen compounds studied, the readiness with which saponification took place was greatly influenced by the neighboring groups. Thus in the intermediate compound, $(CH_3)_2CH—\underset{\underset{C_6H_5—CH—CN\ (2)}{|}}{CH}—CH\ (1)$, (1) is apparently very easily saponifiable, while (2) saponifies with more difficulty. The compound $\begin{array}{l} CH_2—COOH \\ | \\ C_6H_5—CH \\ | \\ C_6H_5—CH—CN \end{array}$ contains a cyanogen group that saponifies with great difficulty, while the compound $\begin{array}{l} C_6H_5—CH—CH_2—COOH \\ | \\ C_6H_5—C—CN \\ | \\ C_6H_5—CH—CH_2—COOH \end{array}$ contains a cyanogen group that appears to resist the ordinary methods of saponification. The influence of neighboring groups, especially the phenyl group, in retarding saponification will be studied in detail later.

Some of the half nitrile of the phenylisopropyl succinic acid was converted to the dibasic acid by heating in a bomb with hydrochloric acid. The resulting mixture was extracted with hot water from which fine, pure white crystals of the phenylisopropyl succinic acid were deposited on cooling. These were recrystallized from benzene containing a little petroleum ether. The acid has a white powdery appearance in the mass but under the microscope shows very minute colorless plates, melting at 178°.

The acid is very soluble in ether, alcohol and acetic ether, moderately soluble in benzene, chloroform and hot water, and almost insoluble in petroleum ether and cold water.

Titration.—0.0868 gram of the acid required 7.80 cc. N/10 sodium hydroxide. Calculated for 2 acid H. in $C_{13}H_{16}O_4$, 7.88 cc. N/10 sodium

hydroxide. Combustion, 0.1238 gram substance gave 0.3005 gram CO_2. This analysis gave: C, 66.2; H, 6.6. Calculated for $C_{13}H_{16}O_4$: C, 66.1; H, 6.8.

Conclusions.—(1) The data here given show that succinic derivatives, made by reactions that leave no doubt as to their composition, are different compounds from the isomers described in the foregoing article. Hence these latter are in all cases glutaric derivatives.

(2) Sodium benzyl cyanide resembles sodium cyanacetic ester in its action with aldehyde cyanhydrines. As in the case of the deportment of benzyl cyanide with cinnamic ester, so here also there is a tendency toward partial saponification. Having determined the deportment of benzyl cyanide in this respect, since we were using benzyl cyanide in the synthesis of alkyl glutaric and succinic acids when the article by Higson and Thorpe appeared, it is not our intention to make any closer approach to the field of work of Thorpe and his pupils.

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INFLUENCE OF FERTILIZERS UPON THE COMPOSITION OF WHEAT.

BY HARRY SNYDER.

Received January 23, 1908.

There are a number of factors which are known to materially influence the composition of wheat as (1) seed, (2) soil, (3) climatic conditions, and (4) storage. These have been studied by a number of investigators, and in general it can be said that while the composition of wheat, like that of all seeds, is fairly constant it is possible by increasing the fertility of the soil, by seed selection, control of the soil moisture, systematic cultivation or irrigation, and by control of the chemical changes incident to storage to favorably influence its composition and nutritive value.

In order to study the influence of fertilizers upon the composition of wheat, sixty samples grown at 12 different localities in Minnesota and fertilized with different kinds of fertilizers were analyzed. At each of the twelve different places where the fertilizer tests were made a uniform piece of land was selected and five quarter acre plots were staked off. Each plot received similar treatment as to cultivation and seeding. On one of the plots no fertilizer was used and on the remaining plots, complete, potash, superphosphate and nitrogen fertilizers were applied. The grain from each of the plots was harvested and threshed separately, and bushel samples were shipped to the Chemical Laboratory of the Minnesota Experiment Station for analysis and milling and technical tests.

Influence on Physical Qualities of Grain.—In many instances the fer-

tilizers exerted some special influence upon the growth of the crop, *e. g.*, nitrogen used alone retarding maturity, and minerals used alone hastening maturity. In some cases size and character of the kernels were influenced by the fertilizers. Larger, better filled, and better colored grain generally, resulted from their use, particularly where the fertilizers perceptibly increased the yield. In eight trials the phosphate fertilizers increased the weight of the grain per bushel and in two trials the weight was the same as when no fertilizer was used. In five trials potash increased the weight per bushel and in no case was the weight decreased by the application of potash. In some cases the nitrogen fertilizer increased and in other cases decreased the weight. In general, the heaviest weight and best quality of wheat was produced on the fertilized plots. In some of the tests, the phosphate, and in others the potash fertilizer exercised the greatest influence upon the quality of the grain, as to weight per bushel and uniformity of kernels. Nitrogen alone did not exert as great an influence toward improvement of the kernels as the mineral elements alone; in a few instances, however, nitrogen alone improved the glutenous character and general appearance of the grain.

From the tests made upon the different soil types of the state it would appear that fertilizers may improve the quality of the grain, but the kind of fertilizer element as potassium, or phosphorus required for purposes of improvement depends entirely upon the individuality of the soil on which the wheat is grown. Improvement in quality of the grain follows as a result of increase in the fertility of the soil, and a soil must be built up in the elements it lacks and these must be ascertained by experiments. In many localities where these experiments were made the climatic conditions were unfavorable, but it was noted that with the more liberal supply of plant food in the fertilized plots the quality of the grain as to weight per bushel, plumpness, maturity, and uniformity of kernels was better than on the unfertilized plots. This would indicate that during unfavorable seasons crops produced upon soils of low fertility are more susceptible to the adverse climatic conditions than crops grown upon soils of high fertility.

INFLUENCE OF FERTILIZERS UPON THE COMPOSITION OF WHEAT.—AVERAGE COMPOSITION.

Kind of fertilizer.	No. of samples.	Moisture. Per cent.	Protein $N \times 6^{25}$. Per cent.	Ether extract. Per cent.	Crude fiber. Per cent	Ash. Per cent.	Nitrogen-free extract. Per cent.
Nitrogen	12	10.03	13.63	2.15	2.74	1.58	69.87
Potash	12	10.24	13.02	2.10	2.65	1.62	70.37
Phosphoric acid	12	10.39	12.65	2.19	2.73	1.73	70.31
Complete (N, K_2O and P_2O_5)	12	10.15	13.17	2.22	2.76	1.69	70.01
No fertilizer	12	10.16	13.04	2.11	2.72	1.64	70.33

In all of the individual tests except one, the highest percentage of nitrogen was secured from the wheat grown upon the plots receiving

either nitrogen alone or the complete fertilizer of which nitrogen formed a part. A similar result was secured in 1905 from a more limited number of trials. Increasing the supply of nitrogen in the soil slightly increased the amount of nitrogen in the grain. As previously noted, this increase in nitrogen alone, unless associated with the mineral elements, may result in a poorer quality of grain, for while nitrogen alone increased the crude protein content of the grain, to secure improvement in quality as well, the nitrogen must be associated with the other essential elements of plant food. The results indicate that in many cases it is possible to increase the protein content of wheat one per cent. or more through the use of fertilizers, also to secure an improvement in quality, although the average increase in protein was small.

The influence of the nitrogenous fertilizers upon the form of the nitrogen in wheat was also studied. A number of investigators have reported the presence of nitric nitrogen in plants. King and Whitson, in the Eighteenth Annual Report of the Wisconsin Experiment Station, page 220, state that in the case of oats in the "milk stage" grown on soil very rich in nitrates, 2.64 per cent. of nitrogen was obtained by the ordinary Kjeldahl method, but when the method was modified to include nitrates, 3.12 per cent. was obtained. They also report nitric nitrogen in corn and potatoes.

For the purpose of determining the amount of nitric and other forms of nitrogen in the wheat fertilized with nitrate of soda, three samples were selected; wheat grown on University Farm, in the central western and in the southwestern part of the state. The results of the analyses are given in the following table:

FORMS OF NITROGEN IN WHEAT FERTILIZED WITH NITRATE OF SODA.

	Wheat from University farm. Per cent.	Wheat from central western part of state. Per cent.	Wheat from southwestern part of state. Per cent.
Nitrogen (Kjeldahl process)	1.90	1.77	2.07
Albuminoid nitrogen	1.78	1.69	1.98
Nitrogen (modified to include nitrates)	2.01	1.86	2.22
Excess of modified over ordinary Kjeldahl process (nitrates?)	0.11	0.09	0.15
Nitrogen as nitrites	0.00006	0.00004	0.00008

The difference between the nitrogen obtained by the modified and by the ordinary Kjeldahl process can not all be considered as nitric nitrogen but when the nitrate of soda was used as a fertilizer a small amount of nitric nitrogen was found by qualitative tests to be present in the wheat. The albuminoid nitrogen and the modified nitrogen determinations show that not all of the nitrogen in the plant was present as proteins. Qualitative reactions of all of the flours made from the wheats fertilized with nitrate of soda and organic nitrogen showed the presence

of nitric nitrogen and also traces of nitrites. Some of the wheats grown upon the plots where there was no nitrogen in the fertilizers gave the same reactions, while others did not. The nitrogen content of the wheat was slightly increased by applications of nitrogenous fertilizers to the soil, but as previously stated the bread-making qualities of the flour from such wheat are not necessarily improved. Similar results have been reported by Hall, of the Rothamsted Station: "Again, as we have seen, 'strength' is generally associated with a high nitrogen content, yet the wheats grown on some of the Rothamsted plots, where so large an excess of nitrogenous manure is applied that even the grain becomes more nitrogenous, instead of becoming stronger only gets incredibly weaker."—*Journal of the Board of Agriculture*, September, 1904, page 332. It is quite evident that the form as well as the amount of nitrogen must be taken into consideration in studying the bread-making qualities of flour.

Influence on Bread-making Value.—Forty-one of the sixty samples of the wheat were milled at the experimental flour mill of the Minnesota Experiment Station. The protein content of the flour was determined, and technical bread-making tests were made by an experienced baker, accustomed to making tests for a large flour mill.

The wheat from three of the nine places, grown upon the plots fertilized with phosphates, produced flour that made the best bread. From two of the places the wheat fertilized with nitrogen made the best bread; from two fertilized with potash, and from two the complete fertilized wheat.

In thirty of the forty-one tests the fertilizers which gave the largest yields per acre produced wheats of the highest bread-making value, while in ten of the tests the best quality of flour was secured from the fertilized wheats which did not show the largest yield per acre. While yield and bread-making quality are both improved by the use of fertilizers they are not necessarily both improved to the same extent by the same fertilizer.

There appears to be no constant relationship between the per cent. of protein in the grain and flour, and the bread-making value, and while it is possible to increase the amount of protein in flour by the use of nitrogenous fertilizers the bread-making value of the flour is not proportionally increased. In many instances the increase in nitrogen content imparted a negative value.

The experiments taken as a whole show that not only the yield of wheat, but also the bread-making value can be enhanced by increasing the fertility of the soil, and that there is a very close relationship between the amount of available plant food in the soil, and the quality of the

wheat produced upon that soil and its bread-making value. Credit is due Mr. L. O. Bernhagen for assistance rendered in the analytical work.

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THE PRECIPITATION METHOD FOR THE ESTIMATION OF OILS IN FLAVORING EXTRACTS AND PHARMACEUTICAL PREPARATIONS.

BY CHARLES D. HOWARD.

Received February 6, 1908.

The polariscopic method for the estimation of essential oils in commercial extracts is of but limited application, the oils of lemon and orange being the only ones that can be accurately determined in this manner. For the estimation of such oils as peppermint, clove, wintergreen, and many others, two procedures are open: (*a*) the application of methods for the estimation of the most important constituents of these oils, such as menthol, eugenol, or methyl salicylate, and (*b*) the method by precipitation as suggested by Mitchell[1] and now adopted with modifications as official by the A. O. A. C.

In most instances the first procedure, as applied to extracts, is obviously capable of affording but little better than a general idea as regards strength or quality, while results by the second process involve the application of a large and variable correction. Thus, in the case of lemon oil Mitchell[2] found that results near to the truth were obtainable only in the presence of a relatively large proportion of oil—a 6 per cent. extract, for instance, showing 4.80 per cent. recoverable, while a 2.50 per cent. extract afforded by this procedure less than one-half of the oil actually present.

With a less proportion of oil the error becomes still greater, and when we consider in addition that this error apparently varies not only with the quantity of oil, but with the kind, it is evident that for the examination of many of the miscellaneous extracts and essences now on the market—many of them containing as they do but one or two per cent. of oil—the method as at present carried out is of but very limited value. This fact will be appreciated by any who has attempted to examine some of the cheaper grades of peppermint essence.

By the modified method here proposed the writer has obtained most excellent results. The procedure has the advantage that no correction whatever for oil retained in solution is necessary, and moreover, with the single exception of almond extract, it affords equally accurate results in the case of alcoholic solutions of almost any one of the large

[1] THIS JOURNAL, 21, 1132 (1899).
[2] *Loc. cit.*

class of essential oils. The advantages of simplicity and rapidity of execution may also be claimed, it being possible to carry through a series of several determinations in ten minutes.

Procedure.—To 10 cc. of the extract, pipetted into an ordinary Babcock milk bottle, are added in the following order, 25 cc. of cold water, 1 cc. hydrochloric acid of 1.2 specific gravity and 0.5 cc. chloroform. The mouth of the bottle is then closed by the thumb and vigorously shaken for not less than one minute. By this means all of the oil is dissolved by the chloroform, while the latter, in saturating the water, apparently serves to displace any appreciable trace of oil otherwise retainable by the alcohol-water mixture. The bottle is now whirled in the centrifuge for one and one-half to two minutes and the resulting clear supernatant liquid is removed to within 3 or 4 cc. by the insertion of a glass tube of small bore connected with an aspirator. To the residue 1 cc. of ether is added and the contents of the bottle well agitated. Holding the latter at a slight angle it is plunged to the neck in a boiling waterbath, and, giving a gentle rotary motion, is maintained at this temperature for exactly one minute. This step is best carried out by removing one of the small rings from a water- or steambath and holding the bottle in the live steam. The ether serves the purpose of steadily and rapidly sweeping out every trace of chloroform—a result that would be otherwise attainable only with considerable difficulty and loss of oil. The latter by this procedure has been found to be inappreciable. Finally the bottle is cooled and filled with water at room temperature so as to bring the oil into the graduated stem of the bottle, and after centrifuging for one-half minute the reading is taken to the highest point of the meniscus; the reading multiplied by 2 gives the per cent. of oil.

If it be desired, a special milk bottle with stem of smaller bore, or a skim milk bottle provided with a straight introductory tube, may be employed. It has been found, however, that with the ordinary Babcock bottle there is no difficulty in securing check results to one-tenth per cent.

Modification for the Heavier Oils.—In the case of oil of wintergreen it was found to be impossible to secure a compact readable column of the oil by means of salt solution. This procedure also proved to be not satisfactorily applicable for almond extract. For the estimation of these oils use was at first made of a specially devised form of the so-called Hortvet tube, in which the bore of the stem is so reduced that the graduated portion contains 2 cc. instead of 5 cc., the subdivisions having therefore the same values as in the case of the Babcock bottle. Using this form of tube, in the case of almond extract the most satisfactory results were obtained by employing double the quantities of chloroform and ether specified. Working in this manner it was found pos-

sible to recover practically 100 per cent. of the oil from a 1 per cent. extract, but with stronger extracts 80 to 90 per cent. only proved recoverable.

In most cases, however, the use of the ordinary Babcock bottle with a suitable heavy liquid will be found to be preferable. For this purpose, except with the oils of cinnamon and cassia, the use of salt solution is out of the question. Trials were made of the applicability of diluted sulphuric acid, diluted glycerol and of sugar solution. The two latter were found to serve well for the lighter oils, but with wintergreen a gravity of not less than 1.2 is requisite and this involves a too high degree of viscosity. On the other hand, diluted sulphuric acid (1–2) was found to answer admirably. While it might be objected that the acid would tend to decompose some of the oils—notably those of clove and cinnamon—and thus afford low results, yet it was found that if agitation is avoided and the temperature of the acid mixture does not exceed 25°, no readable error is involved.

As a result of a large number of trials of this method, it was found that (except in the case of almond extract) not only could practically the theoretical amount of oil be recovered from 1, 3, 5 and 10 per cent. strengths of alcoholic solutions, but that also in the case of lemon and orange extracts results thus obtained very generally agreed to $^1/_{10}$ per cent. with those obtained polarimetrically, if the factor designated by Mitchell and Leach (3.4) was used.

It is well recognized that results by the polarimetric method of examining lemon and orange extracts are not to be implicitly relied upon as indicating in all cases the true proportion of oil present. The use of small quantities of cane sugar in the preparation of these extracts is apparently somewhat more common than has been generally supposed. Without doubt, so-called "washed" or "distilled" oil is being used to some extent in the making of extracts, and furthermore the addition of high polarizing orange turpenes for the purpose of increasing the rotatory power is a perfectly practicable form of adulteration.

The precipitation method, therefore—aside from merely providing material for a refractometric examination—affords a direct and valuable check on the polarimetric results. For instance, if the results by precipitation are materially lower than those obtained polarimetrically, there is ground for the suspicion that other than a "straight" oil has been used; if on the contrary, they are higher and the oil is present in moderately large quantity, such would be proof-positive either of adulteration with a foreign oil, or else of the use of an oil that had undergone marked deterioration, while if the polarimetric reading was but slight, or zero, any precipitated oil might be assumed to represent citral or one of the other lemon oil substitutes.

The results presented below were obtained on solutions of definite strength prepared with 90 per cent. alcohol. Results obtained with commercial extracts are also submitted.

Extract.	Strength. Per cent.	Oil recovered. Per cent.
Lemon	5.0	5.0
"	1.0	1.0
Peppermint	1.0	1.0
"	3.0	3.0
"	5.0	5.0
Clove	1.0	1.0
"	10.0	10.2
Cassia	1.0	1.0
Wintergreen	1.0	1.1
"	2.0	2.0
"	5.0	5.1
Bitter almonds	1.0	1.0
" "	3.0	2.5
Citral (pure, optically inactive)	3.0	3.0
"	0.5	0.5

COMMERCIAL EXTRACTS.

Variety.	Oil by precipitation.	Oil by polarizatior
Lemon	4.8	4.80
"	4.6	4.63
"	4.0	4.10
"	5.0	5.00
"	4.40	4.50
"	4.8	4.70
Peppermint	3.8	....
"	5.6	....
"	12.4	....
Cinnamon	3.0	....
Checkerberry	4.0	....
"	12.5	....
Rose	0.6	....

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A COMPARISON OF TWO TESTS OF RED LEAD.

BY EUGENE H. DUNLAP.

Received March 14, 1908.

The tests generally used for the determination of the amount of free litharge, PbO, in red lead are the lead acetate test and the lead peroxide test. The latter is made in two ways, by the gravimetric and volumetric methods.

We will first consider the lead acetate test. This test depends upon the solubility of lead oxide in a solution of lead acetate. A weighed quantity of red lead is taken, and to it is added, in a beaker, a like quantity of lead acetate crystals dissolved in about 150 cc. of hot water. After

stirring, the solution is brought to a boil, and allowed to boil from ten to thirty minutes. It is then filtered through a tared filter, the residue washed thoroughly, dried, and weighed. The loss of weight between the amount of red lead taken and what remains is the weight of free litharge.

The lead peroxide test can be used in two ways, the gravimetric, which is a direct, and the volumetric, which is an indirect method. We will first consider the gravimetric method. This consists in treating the red lead with nitric acid in a warm solution. The peroxide formed is collected on a tared filter, washed thoroughly, dried and weighed. The amount found is then calculated to Pb_3O_4. The loss between the original sample taken and the amount of Pb_3O_4 found is the weight of the free litharge.

The volumetric method consists of changing the red lead into lead peroxide, heating gently and adding a known quantity of $N/5$ oxalic acid solution, then boiling. This decomposes the peroxide of lead. While still hot, $N/5$ permanganate solution is added until the color remains for a few seconds. The volume of $N/5$ permanganate solution required is deducted from the amount of $N/5$ oxalic acid solution taken, the resulting volume of the $N/5$ oxalic acid solution is calculated to lead peroxide and from that of red lead, Pb_3O_4.

So much for the tests themselves. Now red lead as it is made commercially, no matter by what process, is pig lead carried through the various stages of oxidation until we come to the point where oxidation practically ceases. The oxygen which is used for oxidation is taken from the air at the temperature at which the lead is worked in the furnaces. In some cases the first part of the oxidation is obtained from oxygen given up by chemical compounds in order to produce new chemical compounds. Therefore from the methods of producing red lead, we can readily see that it is impossible to obtain a pure compound, Pb_3O_4. Red lead is therefore not a pure compound, but consists, outside of very slight quantities of impurities such as lead sulphate, silica, oxide of iron, etc., of various oxides of lead, namely protoxide, PbO; sesquioxide, Pb_2O_3; and minimum, Pb_3O_4. Now the sesquioxide, Pb_2O_3, is insoluble in a solution of lead acetate, while on the other hand it is soluble in nitric acid. This is one of the fallacies of both tests, but sesquioxide of lead is not harmful in red lead in connection with its physical properties, and should therefore not be taken into consideration as an impurity.

On the other hand, litharge, or the protoxide of lead, if present in considerable quantity, is objectionable and especially deleterious to the physical properties of red lead. It is on account of this impurity that red lead is tested, as it is beneficial not only as a protection to the

buyers, but also to the manufacturer, who loses profit if a considerable quantity of protoxide of lead is present.

In order to compare more closely the tests of lead acetate, and lead peroxide, I prepared some red lead as pure as I could get it, by boiling with lead acetate solution and very dilute acetic acid, washed it thoroughly, put it through a No. 21 silk bolting-cloth and dried it. After it was thoroughly dry I made an analysis of it by lead sulphate method and obtained an average result of 99.95 per cent. pure red lead.

Part of this sample with the lead acetate test gave average results of 99.98 per cent. Other samples of this red lead were put through the peroxide tests, using different conditions in each case and gave the following results:

No. 1 sample.—10 cc. nitric acid, sp. gr. 1.42, 150 cc. of hot water = 99.16 per cent.

No. 2 sample.—30 cc. nitric acid, sp. gr. 1.42, 150 cc. of hot water = 94.64 per cent.

No. 3 sample.—50 cc. nitric acid, sp. gr. 1.42, 150 cc. of hot water = 89.02 per cent.

No. 4 sample.—50 cc. nitric acid, sp. gr. 1.42, 150 cc. of hot water and boiled = 77.66 per cent.

The above shows that lead peroxide is affected under certain conditions and that it is soluble in the stronger acid and also upon boiling. Therefore, this test is practically useless in the test for purity of red lead and should not be used. The volumetric method depends upon the formation of peroxide, but gave lower results in all the above cases.

Now red lead which is made from the protoxide of lead produced in the formation of nitrite of soda, will, after it comes through the various processes, contain a small quantity of sodium hydroxide and sodium nitrite. The peroxide test in this case, is even more useless than in the case of red lead made by the processes which carries on the oxidation from pig lead to red lead direct in the furnace. The nitrite of soda present acts upon the peroxide of lead and gives even greater solubility than if added after the peroxide is formed.

In the case of the lead acetate test upon such samples of red lead we first neutralize the caustic soda with very dilute acetic acid, and then proceed with the test. Of a quantity of tests made upon red lead containing caustic soda and less than 0.05 per cent of sodium nitrite, the lead acetate test gave results which varied very little, but in the case of the peroxide test the results were quite varied, some showing a difference of about 10 to 12 per cent.

It seems, therefore, that the peroxide test is much less reliable than that with lead acetate.

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NOTES.

Notes on the Separation of Silica and Alumina in Iron Ores.—A reading of G. W. Dean's "Notes on the Determination of Silica and Alumina in Iron Ores,"[1] and "The Determination of Silica in Iron Ores Containing Alumina,"[2] led to a comparison of the three methods outlined in the above-mentioned articles with the sodium carbonate fusion method.

A brief statement of the four methods may not be out of place; they are as follows:

(1) Sodium carbonate fusion. One gram of the sample was treated with concentrated hydrochloric acid and evaporated to dryness twice, then dissolved in hydrochloric acid, the solution filtered and the residue fused with sodium carbonate. The fusion was treated with hydrochloric acid and evaporated twice to dryness and the silica determined as usual.

(2) Double dehydration of ore in hydrochloric acid, solution in same, ignition of the insoluble residue in platinum and re-solution in hydrochloric acid, and silica determined.

(3) Ignition of ore in porcelain with sulphur, solution in hydrochloric acid, and silica determined.

(4) Ignition of ore in porcelain without sulphur, solution in hydrochloric acid containing 1 gram of stannous chloride in 225 cc., and silica determined.

Alumina was precipitated as phosphate.

The ores used were those encountered in routine work and were as follows: (*a*) Brown hematite-limonite mixture, (*b*) brown hematite, (*c*) red-brown hematite mixture.

The following figures are averages of numerous determinations:

	Ores.					
	(*a*).		(*b*).		(*c*).	
Methods.	SiO_2.	Al_2O_3.	SiO_2.	Al_2O_3.	SiO_2.	Al_2O_3.
(1)	7.70	3.11	5.52	1.44	13.31	4.00
(2)	8.90	2.49	6.01	1.15	13.76	3.70
(3)	8.92	2.37	6.00	1.07	14.07	3.44
(4)	8.71	....	6.17	....	14.17	....

The determination of alumina subsequent to (4) was, of course, impossible.

The following figures show the amounts of alumina soluble in hydrochloric acid before the ignition in method (2), and the amounts liberated by the ignition:

[1] THIS JOURNAL, 29, 1208.

[2] *Ibid.*, 28, 882.

Ore.	Al_2O_3. No. 1.	Al_2O_3. No. 2.
(*a*)	0.97	1.53
(*b*)	0.62	0.59
(*c*)	1.48	2.21

Three different ignition temperatures for method (2) were tried on ore (*a*). A low red heat, barely sufficient to redden the crucible bottom, was applied till the filter was carbonized and about half consumed; this gave results as follows: Silica 8.92, alumina 2.48. A moderate red heat, sufficient to redden the crucible (15 g.) clear to the top, and applied till the filter was entirely consumed, gave: Silica 8.88 and alumina 2.51. Igniting to bright redness gave figures much higher on silica and lower on alumina and so discordant as to be totally worthless.

The sodium carbonate fusion being considered a standard method for the determination of silica, it is evident from the above comparisons that ignition methods (2), (3) and (4) are not universally applicable to the accurate determination of silica and alumina in iron ores.

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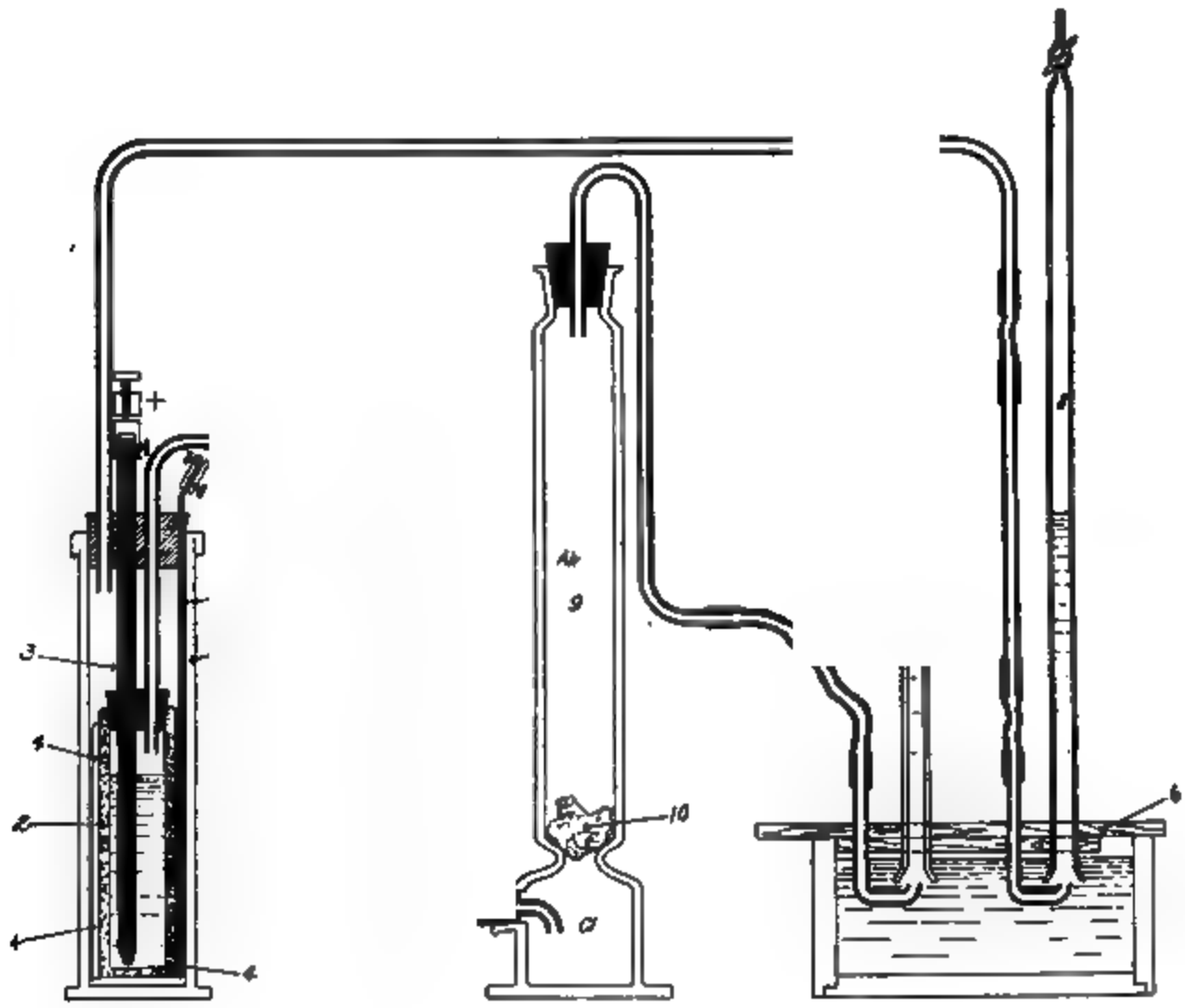
An Apparatus for the Quantitative Electrolysis of Hydrochloric Acid.—A desirable piece of apparatus for a lecture experiment is one that is easily put together for operation, certain to give correct results without any time-consuming preparation or preliminary adjusting. In the opinion of the writer, the following piece of apparatus for demonstrating the volume relation of the hydrogen and chlorine obtained in the electrolysis of hydrochloric acid fulfils the above requirements of "desirable apparatus."

The special points of difficulty to be overcome in an apparatus for this purpose are (1) the mixing of the catholyte with the anolyte; (2) the solubility of the chlorine in the water over which it is to be collected. In the apparatus here described, the mixing of the catholyte with the anolyte is practically entirely prevented by surrounding the anode with a porous cup. The second difficulty is eliminated by discharging the chlorine into the bottom of a tall, large cylinder, and collecting the equal volume of air forced out of the top of the cylinder. These ideas are embodied in the following design.

The electrolysis is carried on in a cylindrical glass jar, *1*; *2* is a cylindrical porous cup; *3*, the carbon anode; and *4* the cathode of sheet platinum. The glass jar and the porous cup are both closed with rubber stoppers, through which are inserted the carbon anode, the platinum wire connection for the cathode, and the delivery tubes. The chlorine delivery tube is fitted with a rubber stopper to the lower opening of

the tall cylinder *9*, and the outlet tube for air is fitted with a rubber stopper to the top of the cylinder. A loose cotton plug *10*, is placed in the cylinder to retard the mingling of chlorine and air. A suitable two-way stopcock interposed as shown at *5* will be found very con-



venient. By means of it the chlorine may be diverted from entering the cylinder, or chlorine may be blown out of the cylinder without disconnecting the apparatus.

The air (or chlorine) and the hydrogen delivery tubes terminate in two small glass tubes, the ends of which are drawn to small openings to discharge the gases in small bubbles. These tubes are fitted into a wooden block by means of which both terminals can be placed under the collecting tubes simultaneously. The rubber tubes which connect the terminals with the main portions of the delivery tubes are made as short as possible, and are coated with shellac, to prevent diffusion, particularly of the hydrogen. Two inverted burettes may serve as collecting tubes.

To start the apparatus, the anolyte is saturated with chlorine by adding some crystals of potassium chlorate to it. The mixture may be used immediately. The anolyte and the catholyte should fill the vessels to practically the same level. After connecting up properly, electrolysis

need be carried on only a minute or two (during which time the chlorine is preferably diverted from entering the cylinder) and then the apparatus is ready for the demonstration.

When put away, the electrolysis vessel, etc., should be filled with distilled water.

I am indebted to Dr. E. P. Schoch, of this laboratory, for the fundamental notions of this design.

J. B. LEWIS.

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A Supposedly New Compound from Wheat Oil.—While engaged in investigating the properties of bleached flours[1] at the University of Nebraska the writer had occasion to extract about 100 cc. of wheat oil from unbleached flour by means of ether. This oil on standing for a short time was observed to deposit a considerable number of small, white crystals. Some of these crystals were removed from the oil by suction and washed on the filter with ether in which they are not readily soluble. The crystals so obtained were oily to the touch and melted to a colorless liquid at 93–94°. By recrystallization from absolute alcohol this melting point was raised to 96.5°.

That the compound contained nitrogen was proven by the usual tests.

Some attempts were made to saponify the compound by boiling with 10 per cent. alcoholic potash but the melting point remained unchanged.

At this point the investigation was broken off, owing to the fact that it was not directly concerned with the bleaching of flours. There was not obtained sufficient of the compound for a complete investigation although it is hoped by the writer to prepare larger quantities in the near future.

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February 16, 1908.

Determination of Phosphorus in Ash Analysis.—In our article in the March number of THE JOURNAL, attention was called to the fact that when the ash of cereals is burned at too high a temperature or fused, the method of determining phosphoric acid by extracting the ash with hot nitric acid gave an apparent loss of the phosphorus, although no appreciable loss in the ash occurred. More recent investigations show that the loss is not entirely due to volatilization of the organic phosphorus as was supposed, but to a conversion of the phosphorus to a form which is not precipitated by ammonium molybdate.

The following results show that even boiling the ash with strong nitric acid for an hour is not quite sufficient to recover all of the phosphorus.

[1] Alway and Gortner, THIS JOURNAL, 29, 1503 (Oct., 1907).

Whenever the ash has been burned at too high a temperature it is necessary therefore to determine the phosphoric acid in the ash by means of the Neumann method (digestion with 5–10 cc. of a mixture of equal parts concentrated sulphuric and nitric acids).

These results show that neither phosphoric acid nor ash is appreciably volatilized on high ignition, but that to recover the converted phosphoric acid from the ash, the Neumann or an equally efficient method must be used.

RESULTS.

	Ash.		Phosphoric acid.			
Sample.	Low redness. (1)	Bright redness. (2)	Hot nitric acid. (1)	Hot nitric acid. (2)	Boiled 1 hr. Nitric acid. (2)	Neumann method. (2)
A.....	2.11	2.08	1.10	0.42	0.99	1.09
B.....	2.18	2.16	1.16	0.48	1.07	1.16

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REVIEWS.

REVIEW OF INORGANIC CHEMISTRY FOR 1907.

BY JAS. LEWIS HOWE.

Received January 13, 1908.

The most important paper which has appeared in inorganic chemistry during 1907 is the lecture which was delivered before the German Chemical Society by Werner, on "The Problems of the Constitution and Configuration of Inorganic Compounds" (*Ber.*, **40**, 15). The subject was treated under five heads, *viz.*: constitution of the metal-ammonia salts; constitutional relations between the metal-ammonia salts and complex salts; relations between the metal-ammonia salts and the hydrates; the special relations of complex inorganic radicals; polynuclear metal-ammonia salts. The paper, which unfortunately does not admit of abstraction within the limits of this review, gives the latest and most comprehensive views of the author, which are winning general acceptation, as offering the only rational theory of the constitution of complex inorganic compounds. The application of Werner's view to many classes of compounds is as yet far from clear or satisfactory, but an important beginning has been made which bids fair to be second only in importance to the doctrine of valence itself.

Two other important papers from a theoretical standpoint have been by Pfeiffer and by Werner on the theory of hydrolysis and the theory of bases (*Ber.*, **40**, 4036, 4133). According to the ideas of these chemists hydroxo-compounds, that is, those containing the undissociated hydroxide group, when treated with acids give salts, not by substitution as generally assumed, but by addition, and the salt formed is primarily an 'aquo' salt, though it may secondarily go over into an anhydrous

salt by the loss of water. Applying this idea in its simplest form we would have for the neutralization of cuprous hydroxide the following: $CuOH + H^+.Cl^- = Cu(OH_2)^+ + Cl^-$. Applying this to the theory of hydrolysis, we have the reaction, $Me(OH_2)X = MeOH + HX$, or $Me(OH_2)^+ \rightleftarrows MeOH + H^+$, in which hydrolysis is conditioned by the tendency of the aquo-metal ion to break up into a hydroxo-compound and the hydrogen ion. According to the theory of Arrhenius, on the other hand, we have the hydrolytic reaction: $MeX + H_2O = MeOH + HX$, or $Me^+ + H_2O = MeOH + H^+$. Here the dissociation of water is the determining factor in hydrolysis, while in the theory of Pfeiffer, it is of little influence. This may be, however, taken account of in the reaction which conditions the basic nature of the hydroxo-compound: $MeOH + H_2O \rightleftarrows Me(OH_2)^+ + OH^-$. Here the water molecule is dissociated in the formation of the aquo-metal ion, the hydroxyl ion being left and imparting the basic reaction to the solution. The strength of the basic character of the hydroxo-compound is thus conditioned upon the tendency of the metal to form aquo-metal ions, and upon the dissociation of water. According to Arrhenius the basic character is independent of the dissociation of water and only dependent upon the dissociation tendency of the metal hydroxide. In Pfeiffer's theory hydrolysis is practically a measure of the tendency of the aquo-metal ion to break up, and of the hydroxo-compound to unite with the hydrogen ion. The application to amphoteric hydroxides is best seen by an example, as of zinc hydroxide:

$Zn(OH)_2$ (base) $+ 2H^+ = Zn(OH_2)_2^{++}$, and

$Zn(OH)_2$ (acid) $+ (OH^-) = Zn(OH)_3^-$.

In his paper on the theory of bases this idea is further developed by Werner and bases are divided into two classes: the anhydro bases which unite with water to form a hydrate which is dissociated in aqueous solution into a complex cation and a hydroxyl anion; and aquo-bases, which comprehend all products formed by the addition of water which dissociate in water giving hydroxyl anions. A number of different classes of anhydro bases exist, as oxygen, nitrogen, phosphorus bases, etc. While the theories of Pfeiffer and Werner have been worked out chiefly in the effort to explain the metal-ammonia bases, they bid fair to throw much light on the more general reactions of inorganic chemistry. The above is but a bare outline and the original papers will well repay a careful perusal.

That which may prove to be the most important inorganic research of the year is one which has been presented as yet only in two preliminary papers by Sir William Ramsay and Cameron (*J. Chem. Soc.*, **91**, 1266, 1593). By the action of a large quantity of radium (87.7 mg.) as bromide and sulphate on water, a mixture of hydrogen and oxygen was obtained. On explosion, a small quantity of hydrogen and emanation remained. An important characteristic of this emanation is its rapid decrease in volume, which seems to point to a chemical change, perhaps into a diatomic gas. A calculation of the life of radium points to a period of only 236 years, a lower value than that found by Rutherford and others. The attempt to account for the excess of hydrogen led to most remarkable results. With the thought that if the emanation acted on the salt of a heavy metal, this would be liberated instead of hydrogen, a solution of copper sulphate was submitted to the action of radium. No copper was

deposited, but on removal of the copper, lithium was recognized in the solution by the spectroscope. Numerous experiments were carried out, with every possible precaution against error, but each time with similar results. A small quantity of sodium seems also to be formed. When lead nitrate is used in the place of copper sulphate, only sodium seems to be present. An examination of the evolved gases showed that from the emanation alone helium is formed, in the presence of pure water, neon, while in the presence of copper sulphate the gaseous product is argon, with no trace of either helium or neon. The suggested explanation of these remarkable phenomena is that the α-particles are, contrary to the view of Rutherford, not identical with helium, but when they collide with the atoms of the emanation, if nothing but the emanation is present, helium results. If, however, the emanation is mingled with the heavier water molecules, the decomposition does not go so far, and neon is the result. In the presence of the still heavier copper atoms, the decomposition remains at argon. By the action of the α-particles atoms seem to be decomposed into other atoms of the same group, thus copper is broken up into sodium and lithium. The authors also find that a solution of thorium nitrate produces continuously minute but clearly detectable quantities of carbon dioxide. The importance of these experiments in opening up new lines of research can hardly be overestimated. In this connection may be noted the work of Boltwood (*Am. J. Sci.* (4), **22**, 537; **24**, 370) on the relation of radium to uranium in carnotite. From the fact that the amount of radium obtained in a given time from uranium is less than theoretically would be formed if radium is an immediate product of uranium, the formation of an intermediate product seemed probable. This was found in carnotite, and at first supposed to be identical with actinium, but further investigation showed that it could be separated from actinium, and that it differs from it in several important particulars. It seems without doubt to be a decomposition product of uranium and the progenitor of radium. Boltwood proposes for it the name *ionium*.

It has been suggested by Coblentz (*Jahrb. Radioaktiv. u. Elektronik*, **3**, 397) that it should be possible to determine whether water is present in crystallized compounds as water of crystallization or as so-called water of constitution, by the presence or absence of the absorption bands of water in the infra-red spectrum. The results obtained from a number of minerals and compounds gave results quite in accordance with the ordinarily received ideas on the subject, but there were also results which were anomalous, such as the presence of water of crystallization in cane sugar, though not in *d*-fructose and *d*-raffinose. Similarly absorption bands for the hydroxyl group were found in talc but not in serpentine. The method seems to offer possibilities of throwing light upon molecular structure, but needs much further investigation.

The subject of isomorphism continues to attract some attention, especially in its connection with molecular volume. Gossner (*Z. Kryst.*, **43**, 130) concludes that isomorphous substances, while in general not possessing the same molecular volume, do not differ to any considerable extent. If there is much difference in molecular volume, the series of mixed crystals will not be continuous. In another paper (*Ber.*, **40**, 2373) he compares the members of the series of double alkali sulphates

of nickel, cobalt, copper and zinc, and also the fluosilicates of the same metals. In the latter case the nickel and zinc salts have nearly the same molecular volume and form a continuous series of mixed crystals, while the cobalt and copper salts differ considerably in molecular volume and there is a break in the series of mixed crystals from 10–30 per cent. of the cobalt salt. In considering the isomorphism of the elements, Tammann (*Z. anorg. Chem.*, **53**, 446) holds that Mitscherlich's rule that similarly constituted compounds are isomorphous cannot apply, because we know nothing regarding the constitution of the elementary molecule, and he concludes that those elements which are chemically analogous are isomorphous. In general, elements of the same group in the periodic system form mixed crystals and not compounds, but occasionally elements of different groups form a much more marked series of mixed crystals than those of the same group. This is particularly apt to be the case when the elements in question are chemically similar and have high melting points. Indeed, the temperature of crystallization seems to be even more important in determining the power of elements to form mixed crystals than is chemical analogy. As a rule, elements of high melting point separate out as mixed crystals, while those of low melting point crystallize as the pure metal. If the melting point of both the metals in a binary mixture is high, a complete series of mixed crystals may be expected to separate.

Fused salt mixtures have been largely studied from a thermometric standpoint, but Shemchushny (*J. Russ Phys. Chem. Ges.*, **38**, 1135) has recently begun an investigation of the microscopic structure of fused salt mixtures, by etching with an appropriate solvent the polished surface of the solid melt. From the study of several series of binary mixtures, such as those of potassium chloride-potassium chromate, he concludes that the micro-structure of salt mixtures differs little from that of metallic alloys.

An interesting case of the action of light, which seems to be recognized for the first time, is described by Alefeld (*Z. wiss. Phot.*, **4**, 364; *Chem.-Ztg.*, **30**, 1087, 1127). In his earlier experiments, a solution of colophonium was spread thinly on a glass plate and dried for fifteen minutes at 100°. The plate was then exposed under a photographic negative for half an hour to direct sunlight. On heating the negative more highly, a clear positive appears on the plate. This action was strongest on exposure to blue light, and careful experiments showed that it was not due to the action of heat. The experiments were later extended and it was found that practically any solution could be used, those giving the best results which leave the most highly colored ash. The solutions may be dried sufficiently before exposure to the light to have the negative placed directly against the plate, but if dried too hard, no change is effected by the light. The action seems to be due to the migration of the molecules from the shaded portions of the plate to those exposed to the light. The best results are obtained by the use of such varnishes as are used as menstrua in porcelain painting. Forty-five different elements were tested and found to be susceptible to this action of light. It is thought that practical application of this phenomenon can be made in the transference of photographs and other designs to porcelain and glass.

That manganese is perhaps the best excitant in luminous paint has

long been known. It now appears from the investigations of Karl (*Compt. rend.*, 144, 841) to play a similar part as regards triboluminescence. If zinc sulphide is heated in an electric furnace with one-sixth its weight of manganese nitrate to 1200°, the resulting crystalline mass, after powdering and washing, shows a remarkably strong triboluminescence, visible even in the daylight. The mass, however, does not exhibit the phenomenon of phosphorescence at all. The manganese nitrate can be replaced by other manganese salts, and even by the oxides of tin, silicon, zirconium, titanium, etc., and triboluminescence ensues, but it does not seem possible to replace the zinc sulphide by even zinc oxide.

Quite an extensive paper by von Hasslinger on the nature of metallic and electrolytic conductivity has appeared in the *Monatshefte* (28, 173). Considering the criteria by which metallic elements are distinguished from the non-metallic, he notes that increase in metallic properties accompanies increase in atomic weight, and it also accompanies an increase in temperature. Thus, sulphur becomes almost black and far less transparent at high temperatures, and those forms of carbon which are most like metals are formed at high temperatures. It may be assumed as probable that all the elements could be brought to the same degree of metallic character by properly choosing the temperature for each. At absolute zero, on the other hand, all substances would become non-metallic, and non-conductors of electricity. The distinction between metallic and electrolytic conductors is rendered more difficult from the fact that decomposition products cannot always be detected in the latter case, nor can the conductors be distinguished by their temperature coefficients. If, however, a metal is in contact with a substance in which its ions can exist, it will show a solution-tension which is recognizable by the development of an electromotive force. Conversely, in such a case the presence of an electromotive force indicates that the conductivity is electrolytic, while no electromotive force is developed if the conductivity is metallic. From this standpoint we must conclude that iodine, and even sulphur are electrolytic conductors. Some substances, as for example, silver sulphide, are electrolytic conductors at ordinary temperatures, and metallic conductors at lower temperatures, and since no abrupt change from one form of conductor to the other can be observed, it follows that both kinds of conductivity may exist side by side. This transition from one form of conductivity to the other is exhibited in carbon, where the conductivity increases with the temperature up to a certain point, and then on further heating decreases. Developing the subject further, the author concludes that there is a practical similarity in the two kinds of conductivity, the number of ions in metallic conduction being very great, and their motion very rapid.

In order to determine the degree of dissociation of fused electrolytes, Arndt (*Ber.*, 40, 2937, 3612) has used fused boric oxide as a solvent. The conductivity of this at 900° is very small ($k=0.000,021$). When sodium metaphosphate is dissolved in this solvent, the equivalent conductivity is found to decrease with decreasing concentration. Taking into account the increasing viscosity with decreasing concentration, it appears that the equivalent conductivity is independent of the concentration. This is most simply explained by assuming that the fused sodium metaphosphate is completely dissociated, so that there is no

further dissociation on further dilution with boric oxide. Arndt believes the same to be the case with all fused electrolytes which are made up of univalent ions.

A clear and comprehensive review of the whole subject of non-aqueous solutions is given by Carrara in the *Gazzetta* (**37**, 1, 525), which is fully abstracted in the *Chem. Zentralbl.* (**1907**, 2, 1576). It is the conclusion of the author that between aqueous and non-aqueous solutions a great similarity exists, but in non-aqueous solutions the phenomena are attended by many and most diverse complications. In the meantime the accumulation of data regarding these solutions must be carried on before generalizations are possible.

Beckmann and his pupils continue (*Z. anorg. Chem.*, **51**, 236; **55**, 371) their work on the accumulation of these valuable data. Using quinoline as a solvent the boiling point method gives normal molecular weights for the halide compounds of zinc and cadmium, while the values for cuprous chloride show increasing association toward Cu_2Cl_2 with increasing concentration, but indicate the simple formula at infinite dilution. Cobalt and nickel chloride and bromide show little tendency toward association even in concentrated solutions, and their compounds with quinoline give normal molecular weights. Phosgene, giving double molecules for acetic and benzoic acids, belongs to the class of weakly dissociating solvents. In it iodine (I_2), iodine trichloride, arsenic and antimony trichlorides, antimony pentachloride and S_2Cl_2 give normal molecules. The S_2Cl_2 molecule is also normal in a solution of ethyl chloride and in liquid sulphur dioxide. In all three of these solvents sulphur dichloride shows abnormality. In the first two its molecular weight is respectively 147 and 130, while that of SCl_2 would be 103. In liquid sulphur dioxide the molecular weight of sulphur dichloride is 226, greater than that required for the molecule S_2Cl_4 (206). In this last solvent potassium iodide was found to have the doubled formula, as previously determined by Walden.

Group I.—A very full investigation of the oxides of the alkali metals has been given by Rengade in *Compt. rend.* (**143**, 592, 1152; **144**, 753, 920; **145**, 236), and summarized with additions in *Ann. chim. phys.* ((8), **11**, 348). When the metals of the alkalies are heated in the air they burn to higher oxides, but if insufficient oxygen is furnished to burn the metal completely to the normal oxide, this seems to dissolve in the excess of metal. By heating in a vacuum this excess may be distilled off, leaving the normal oxide in a crystalline condition, often, as in the case of rubidium oxide, in comparatively large octahedra. Sodium oxide, Na_2O, is white and hardly changes its color on heating; potassium oxide, white when cold, becomes clear yellow at 200°; rubidium oxide is pale yellow when cold and golden yellow when heated, while caesium oxide is orange-yellow cold and darkens on heating to carmine-red, purple-red, and at 150° black. The oxides are somewhat volatile on heating and above 400° melt and decompose into the metal and the dioxide. They are similarly decomposed in liquid ammonia, the sodium oxide least readily, and the compound of the metal with ammonia reacts in turn with the dioxide forming the amide and the hydroxide. By hydrogen the oxides are converted into an equimolecular mixture of hydroxide and hydride, and on heating to 300° in a vacuum the latter is decomposed. The halogen

elements react with the oxides only when warmed. The reaction then becomes violent. The same is true of many other reagents such as sulphur and sulphur dioxide, while hydrogen sulphide reacts violently in the cold. Boron and carbon react only above 400°. Dry carbon dioxide is absorbed at about 300°. Caesium and rubidium oxides absorb the vapor of their metals at ordinary temperature in a vacuum, but the metal distils off on heating to 60° or 80°. Potassium oxide absorbs potassium vapor less readily and sodium is not absorbed by its oxide. On warming in the air, higher oxides are formed, giving in the case of rubidium and caesium the dioxides, trioxides and tetroxides, all of which were prepared and are described. As regards the heat of formation, they vary from 82.4 cal. for Rb_2O to 97.7 cal. for Na_2O. The heat of formation thus does not increase regularly with the molecular weight. The work of Rengade fills an important gap in the chemistry of the alkali metals. With this should be mentioned the work of de Forcrand on lithium oxide (*Compt. rend.*, **144**, 1321, 1402). This oxide was prepared by heating the pure hydroxide in a current of hydrogen at 780°. It can also be prepared by using lithium carbonate in the place of the hydroxide. At this temperature lithium oxide has a very low vapor pressure, but at higher temperatures it volatilizes appreciably.

There are numerous references in chemical literature to the formation of a copper peroxide by different methods. These and other methods have been investigated by Moser (*Z. anorg. Chem.*, **54**, 121) with the result that the only instance in which the peroxide is formed is when a 30 per cent. hydrogen peroxide solution is added to a fairly concentrated (2*N*) copper sulphate solution. There is an immediate precipitation of a yellowish green copper peroxide, which seems to have the formula $CuO_2.H_2O$. To avoid the presence of the acid formed in the reaction, Moser found it best to use instead of copper sulphate a suspension of finely divided copper hydroxide. In this case the peroxide is brown, seems to be crystalline, and may be washed clean by ice water. The product is decomposed by boiling water, and more violently by alkalies, and dissolves easily in acids with decomposition. It also breaks up when in a moist condition, but more slowly when dry. Its rapid decomposition by alkalies explains why Moser could not obtain it by oxidation of copper in alkaline solution or suspension with chlorine, and also why it cannot be prepared by the action of sodium peroxide. However, Müller in reviewing Moser's work (*Ibid.*, 417) finds that if a copper solution is treated with very strong (13*N*) sodium hydroxide solution and allowed to stand for several months, a small amount of copper goes into solution, and that if chlorine then be led into the solution the peroxide is formed, but begins to decompose as soon as the current of chlorine is stopped, the original blue color of the solution being restored. The peroxide is also formed when a concentrated alkaline solution of chlorine acts on metallic copper. The method of Moser, however, seems to be the only way to prepare the peroxide, which must be considered as a very unstable compound. Müller also calls attention to the fact (*Z. Elektrochem.*, **13**, 25) that on the electrolysis of a very strongly alkaline (12–14*N*) solution of copper hydroxide there is formed at the anode a dirty yellow copper peroxide which seems to have the formula Cu_2O_3. This may be

also formed on a copper anode as an orange-red or yellow coating by the electrolysis of concentrated sodium hydroxide.

Group II.—According to Glassmann (*Ber.*, **40**, 3059) the only compound in which the bivalence of glucinum is above question is the acetylacetonate. Glassmann has now prepared glucinum picrate by the neutralization of picric acid in aqueous solution with glucinum carbonate. The normal salt is formed which is soluble in numerous organic solvents. The determination of its molecular weight by the cryoscopic method in acetophenone confirms the bivalence of glucinum, which only among French chemists seems to be seriously doubted. By the action of water, glucinum picrate is converted into a basic salt.

Lohnstein (*Z. Elektrochem.*, **13**, 613) has described a passive state of metallic magnesium. The metal, which is rapidly soluble in dilute acetic acid, as in most acid and even neutral solutions, if immersed in acetic acid to which a sufficient quantity of potassium bichromate has been added, is not attacked at all, but seems to be in a 'passive' condition. Solution and evolution of gas begin immediately if the metal is made the anode of a cell in which the electrolyte is an acetic acid solution of the bichromate. The stronger the acetic acid, the more potassium bichromate is needed to induce the passive state, although small quantities reduce the action of the acid on the metal. The passive state disappears with the addition of chlorides and sulphates to the solution, and the metal dissolves in proportion to the amount of these salts which has been added. Lohnstein thinks that these phenomena are due to catalytic processes.

In a paper before the British Association (*Chem. News*, **96**, 100) at the Leicester meeting, the properties of calcium, especially in its relations to other metals, were discussed by Pratt. Owing to its large atomic volume, calcium has, even in small quantities, a marked influence upon the physical properties of other metals. The chemical activity of those metals which are easily attacked by reagents is much increased by alloying with calcium, and in many cases the alloy is more active than either of its components. The action of calcium upon metals of large atomic volume is greater than upon those of lesser volume. This may be a general principle, and not merely applicable to calcium alloys. Calcium alloys do not give promise of much industrial application, except as far as possibly small quantities of the metal may be used for purposes of hardening, but calcium bids fair to have an extended industrial value in the metallurgical purification of other metals.

Two compounds containing three metals, $NaKHg_2$ and NaCdHg, have been prepared by Jänecke (*Z. physik. Chem.*, **57**, 507), the first of the kind. These compounds were discovered by a study of the melting and solidification points of different mixtures of the metals. The compounds have higher melting points than any of the binary alloys which come near them in composition, the former melting at 188° and the latter at 325°. Jänecke has also (*Ibid.*, **58**, 245) confirmed the work of Kurnakow on the compounds of potassium with mercury, and finds the melting point of KHg to be 178° and that of KHg_2 279°. The three compounds whose formulas were not definitely determined by Kurnakow, Jänecke finds to be K_3Hg_9, melting point 204°; K_2Hg_9, 173°; and KHg_9, 70°. Kurnakow (*Z. anorg. Chem.*, **52**, 416) has extended his observations to the amalgams

of rubidium and caesium, and finds here also as characteristic the mercurides corresponding to $NaHg_2$ and KHg_2. In addition to $CsHg_2$ (melting point 208.2°) $CsHg_4$ and $CsHg_6$ were found, with melting points 163.5° and 157.7°. As far as examined the rubidium curve resembled that of caesium. Kurnakow calls attention to the fact that the formulas $M'R_2$, $M'R_4$ and $M'R_6$ seem to be characteristic for mercurides and cadmides.

Although appearing in THIS JOURNAL (29, 844) the work of G. McP. Smith on ammonium amalgam should not be omitted from this review. After examining the three views of the constitution of this much-studied substance; that of Berzelius, supported by LeBlanc, that it is a compound of mercury with the metallic radical NH_4; that of Moissan that it is an ammonia compound of mercury and hydrogen; and that of Rich and Travers that it consists of free ammonium NH_4, dissolved in mercury, Smith shows conclusively that it must be considered exactly analogous to the amalgams of the other alkali metals, the radical NH_4 acting as an alkali metal. The work of Coehn, indeed, where copper, cobalt and zinc salts were precipitated by ammonium amalgam, would be sufficient to establish this view, were there not a possibility that this precipitation might be due to nascent hydrogen, formed in the decomposition of the amalgam. Barium and potassium are not precipitated by nascent hydrogen, but Smith, on treating ammonium amalgam with barium and potassium salts, effected an exchange between the ammonium of the amalgam and the barium and potassium ions. The amalgam is thus a solution of a very unstable compound, $(NH_4)Hg_m$, in mercury and is properly called ammonium amalgam. At about zero it begins to break up into mercury, ammonia and hydrogen, and the entangling of these gases in the mass causes the familiar frothing, which is not a property of the compound but a phenomenon of its decomposition.

Early in the year there was published a posthumous paper (*Compt. rend.* **144**, 593) by Moissan regarding a property of platinum amalgam. When the amalgam is shaken with water there is formed a semi-solid, buttery mass, which exceeds the original volume of the amalgam several times. This emulsion, for such it seems to be, is stable at 100° and at —80°. Platinum amalgam forms a similar emulsion with sulphuric acid, ammonia, salt solution, glycerol, acetone and many other organic liquids, but not with benzene. The simplest method of preparing this emulsion is to shake 2 cc. of mercury with 12 cc. of water to which a few drops of a 10 per cent. solution of chlorplatinic acid have been added. Lebeau (*Ibid.*, 843) gives further particulars received from Moissan regarding the amalgam. The amount of platinum necessary to produce the emulsion phenomena is very small. It is quite noticeable when a 0.038 per cent. amalgam is used, and the best results are obtained when about one-half of 1 per cent. platinum is present. The amalgams of the other metals of the platinum group show no tendency to form similar emulsions. The presence of amalgams of other metals, such as zinc, tin, lead or calcium, destroys the emulsifying power. The emulsion with a 5 per cent. gelatin solution shows under the microscope a structure similar to that of a soap foam, in which the air is replaced by the liquid. It was noticed that in forming an emulsion with platinum amalgam and ether, if the tube in which the amalgam was shaken was closed by the finger, no emul-

sion was formed, but if a clean, dry cork stopper, or better a rubber stopper was used, the emulsion was readily formed.

Group III.—No inconsiderable amount of work has been done upon the rare earths, but little of this work calls for notice here. Barbieri (*Atti. accad. Lincei Roma* (5), **16**, 1, 399) has studied the properties of several of the rare earths as catalytic agents, using as tests the reaction between nitric acid and oxalic acid, and that between potassium permanganate and oxalic acid. In the former reaction ceric salts act much like those of manganese as catalyzers, lying in this respect between manganese and iron. Incidentally it was found that cobalt salts lie between those of iron and nickel. Salts of lanthanum, praseodymium, neodymium, and yttrium have no influence upon the reaction. By measuring the time of reduction of potassium permanganate in sulphuric acid solution of oxalic acid, the order of catalytic action was found to be manganese, cerium, cobalt, praseodymium, neodymium, lanthanum and nickel. Here again cerium lies close to manganese, which reminds the author of the observation of Mendeléeff that in the rare earths one seems to see analogues of the members of the iron group, especially as cerium in many respects resembles manganese. This seems a rather remarkable prediction in the light of the chemical knowledge at the time it was written. By the fractional crystallization of ytterbium nitrate from nitric acid, Urbain (*Compt. rend.*, **144**, 759) has succeeded in decomposing it into neo-ytterbium with atomic weight close to 170, and a small quantity of a new earth, for which Urbain proposes the name lutecium, Lu, derived from the old name of Paris. The atomic weight of lutecium is not much above 174.

Electric furnace products. Du Jassonneix has continued his researches upon the borides, adding quite a number to those already prepared (*Compt. rend.*, **143**, 897, 1149; **145**, 121, 240; *Ber.*, **40**, 3193). In his work with chromium he finds that chromium oxide can be reduced by boron only in the electric furnace, and that while two definite compounds exist, Cr_3B_2 and CrB, they can be isolated only when one starts out with an almost homogeneous melt of nearly the desired composition. Boiling acids attack these compounds with ease, and the second one is acted on in the cold. By using the thermite process, Wedekind (*Ber.*, **40**, 297) has also prepared a boride of chromium which has a composition near CrB, but has a lower specific gravity and decidedly greater resistance to acids than the boride prepared by du Jassonneix. The oxides of manganese are readily reduced by boron in the electric furnace, the products being MnB_2 and MnB. The latter only is magnetic, contrary to the opinion of Wedekind, and is easily attacked by acids. It has been supposed that the green flame with which the evolved hydrogen burns when borides are attacked by acids, is due to the presence of an unisolated hydrogen boride, but du Jassonneix considers that it is merely due to the presence of traces of boric acid, or in cases to boron chloride. In addition to the iron boride, FeB, prepared by Moissan, du Jassonneix has prepared both Fe_2B and FeB_2; they are formed by the direct union of reduced iron and boron, the former either in the electric furnace or in a gas furnace, the latter in the electric furnace only. FeB_2 is very resistant. The only borides of cobalt and nickel that could be prepared are Co_2B, Ni_2B, CoB_2 and NiB_2. These can be formed by heating a mixture of the elements in a current of hydrogen at 1100–1200°. Wedekind's researches (*Ibid.*, **40**, 1259) were

chiefly with reference to the magnetic properties of the borides. He found the pulverulent manganese boride, MnB, to be half as strongly magnetic as powdered iron, while in compact form it was about one-fourth as magnetic as iron. Manganese antimonide, MnSb, is more magnetic than the boride, and the phosphide, Mn_3P_2, is also magnetic. The boride of manganese is recommended by Hoffmann (*Z. angew. Chem.*, **19**, 2133) as superior to the boride of iron for the preparation of boron sulphide. The manganese boride is heated in a current of hydrogen sulphide to about the melting point of antimony. The boron sulphide, when heated in hydrogen sulphide, fuses and on cooling gives a vitreous modification, different from either the crystalline or amorphous. This vitreous modification is more stable in the air than the others but like them is decomposed very rapidly by water into boric acid and hydrogen sulphide.

In the preparation of zirconium carbide, Moissan used the pure oxide and sugar carbon, and found the reduction difficult with a current of 1000 amperes. Wedekind finds (*Chem.-Ztg.*, **31**, 654) that by using the natural oxide and pure coal, zirconium carbide is readily formed by prolonged heating at 600 amperes. The fused or sintered mass is very resistant to water, air and hydrochloric acid, but not to concentrated nitric or sulphuric acid. It thus fully resembles Moissan's carbide. This zirconium carbide, ZrC, is an excellent conductor of electricity and Wedekind suggests its use as electrodes. On heating in nitrogen, the nitride is formed, but no cyanide.

In order to determine whether it were possible to prepare a silicide of copper, richer in silicon than Cu_4Si, Vigouroux (*Compt. rend.*, **144**, 917) heated a mixture of copper and excess of silicon in the presence of lead, bismuth and antimony, in a current of hydrogen for three hours at 1200°. The copper silicide formed distributed itself differently in the different metals, but in every case the limit was reached with 10 per cent. of silicon, corresponding to Cu_2Si. Another method of investigation of these silicides was that of Rudolfi (*Z. anorg. Chem.*, **53**, 216), who fused together copper and commercial silicon and studied the product as an alloy. Account was taken of the iron present in the silicon as Fe_2Si, and in preparing the richer silicon alloys, an alloy with low silicon content was used, in the place of pure copper. The quantities were so chosen as to give the same volume (5 cc.) of alloy in each case, and the temperatures used were the melting points of antimony, gold and nickel (630.6°, 1064°, 1451°). Two distinct compounds were found, Cu_3Si and $Cu_{19}Si_4$. Up to 5 per cent. silicon the alloys are ductile, but the higher the content of silicon, the more frequently is annealing necessary. Under 5 per cent., the alloys are about as hard as copper, but from 5–10 per cent. silicon, they increase in hardness very rapidly. Above this the hardness increases very slowly until 60 per cent. is reached; the alloys with above this amount of silicon are of approximately the same hardness as pure silicon. The hardness is not appreciably increased by chilling. The red color of copper is very materially lightened by even traces of silicon, the 1 per cent. alloy being brass yellow, while the 6–10 per cent. alloys are silver white. With more silicon the steel-gray color of silicon is gradually approached.

$MoSi_2$ and WSi_2 have been prepared by Defacqz (*Compt. rend.*, **144**, 848,

1424) by fusing copper silicide with metallic molybdenum or tungsten in the electric furnace. These silicides are very stable when heated in the air and very resistant to all acids except to the hydrofluoric-nitric acid mixture, and also to fused acid potassium sulphate, but they are easily attacked by hot chlorine and fused alkalies. The WSi_2 may also be prepared by the reduction of a mixture of silica and tungstic acid with aluminum. Hönigschmid has also prepared (*Monatsh.*, **28**, 1017) $MoSi_2$ and WSi_2 by this method, as well as $TaSi_2$, which resembles the others except that it is somewhat soluble in hydrofluoric acid. Quite similar but less resistant is manganese silicide, Mn_3Si_2, prepared by Gin by the reduction of rhodonite in the electric furnace. Lebeau, however (*Compt. rend.*, **143**, 1229; **144**, 85) thinks Gin's product is not pure Mn_3Si_2 but an impure Mn_2Si. Wedekind calls attention to the fact that the silicide of manganese is never magnetic (*Ber. physik. Ges.*, **4**, 412) while manganese forms magnetic compounds with most of the other moderately negative elements. Thus manganese carbide when prepared in the electric furnace is magnetic and the same is true of the nitride when it has been very highly heated. At a high temperature the unmagnetic MnAs changes into the magnetic Mn_2As; some of the numerous manganese phosphides are magnetic, others not; the bismuthide (MnBi?) is strongly magnetic although bismuth is typically diamagnetic. Wedekind considers that these facts, together with the fact that numerous compounds of chromium, cobalt and nickel, as well as those of iron are magnetic, prove that magnetism is not merely an atomic property, but also a property of molecules. The only other new silicides prepared during the year are PtSi, made independently by Lebeau (*Compt. rend.*, **145**, 241) and Vigouroux (*Ibid.*, 376) by fusion of the constituents in the electric furnace, and the double silicide, Cu_2PtSi, prepared by the latter by fusing platinum with copper silicide.

The preparation of nitrides possesses an industrial importance from the fact that they yield ammonia on hydrolysis, and hence numerous patents have been taken out along this line. It has long been noticed that nitrogen is much more rapidly absorbed by calcium carbide when in the presence of calcium chloride, and this idea is covered by patents. Going out from the fact that calcium chloride is hygroscopic and its presence may give rise to the formation of acetylene and thus occasion dangerous explosions, Carlson proposes (*Chem.-Ztg.*, **30**, 1261) to replace the chloride by fluorspar, which he claims gives equally good results. Bredig has taken up the investigation of this catalytic action of calcium chloride (*Z. Elektrochem.*, **13**, 69, 605), and finds that at the temperature of 800° the absorption of nitrogen is very much increased by the presence of 10 per cent. of the chloride, and that the other chlorides of alkalies and alkaline earths also have an accelerating action, but much less marked than that of calcium chloride. While the fluorides, oxides, phosphates and sulphates have some accelerating action, it is also far less than that of the chlorides. From the fact that the free metals, calcium, magnesium and sodium, have little catalytic action, Bredig concludes that the hypothesis that the action is primarily an absorption of nitrogen by the free metal, cannot be true. The fact that the absorption is so little increased by the presence of the easily fusible chlorides, such as those of lithium and potassium, seems to show that the increased action is not due merely to a lowering of the melting point. It is un-

questionably dependent upon the specific nature of the added substance. The results of Bredig are in the main confirmed by those of Foerster and Jacoby (*Ibid.*, 101), except that they find that calcium fluoride has a much more marked action than was found by Bredig, but this action does not become manifest to an appreciable extent until the temperature of 900° is reached. They recommend the use of fluorspar, but a somewhat higher temperature is necessary than when the chloride is used. Fischer (*Ber.*, **40**, 1110) suggests the use of the calcium carbide-chloride mixture in the preparation of argon from the atmosphere, oxygen being absorbed with the formation of oxide and carbon, the nitrogen with the formation of calcium cyanamide and carbon. By circulating air over the mass at 800° crude argon is rapidly obtained. Fichter (*Z. anorg. Chem.*, **54**, 322) would make use of crude aluminum nitride for the preparation of ammonia. The nitride is made by heating aluminum bronze and a small quantity of carbon in the form of soot, in a current of air. To obtain a pure aluminum nitride nitrogen and not air must be used. The nitride is decomposed very slowly by the moisture of the air, but rapidly by heating with an alkaline solution. Serpek has taken out German patents (Kl. 12.181991–2) for the preparation of aluminum for the manufacture of ammonia, by heating a mixture of aluminum carbide and a small amount of carbon in the air. The nitride obtained readily gives off almost all its nitrogen as ammonia with boiling water. In his second patent Serpek recommends the addition of a very small quantity of hydrochloric acid gas or sulphur dioxide to the nitrogen, for the purpose of accelerating its absorption by the calcium carbide.

Group IV.—Some preliminary experiments have been described by Parsons (*Proc. Roy. Soc.* (*A*), **79**, 532) on the effect of high temperature and pressure on carbon. Coal was subjected to a pressure of 30 tons to the square inch and a current varying from 6000 to 50,000 amperes at two volts. In spite of cooling, the steel walls were somewhat fused. The carbon was in every case changed to soft graphite and no trace of diamonds was found. In the effort to prevent erosion of the walls of the cylinder the carbon was packed in magnesia, but this was quickly converted into magnesium carbide. Even at a pressure of 100 tons and a current of 12 volts and 100 kilowatts no diamonds could be found. When carbon was heated with carbon dioxide, the monoxide was almost exclusively formed. Incidentally it was found that at a pressure of 30 tons to the square inch, liquid carbon dioxide is compressed to one-fifth of its volume.

The investigation of complex carbonates, which was begun several years ago by Reynolds, has been extended by Wood and Jones (*Proc. Cambridge Phil. Soc.*, **14**, 171) to many new metals. The precipitate formed by potassium carbonate with solutions of most metals is soluble in excess, but this solution is decomposed on boiling. If, however, potassium bicarbonate is added, the solution is stable. In many cases, as with cobalt, copper, nickel, ferrous manganese, uranium, zinc, cadmium, bismuth, calcium, silver and magnesium salts, a crystallized double salt is deposited on standing. The general formula of these salts of the bivalent metals is $K_2M''(CO_3)_2.4H_2O$, but no copper salt of this formula was obtained, although it has been described by Reynolds. The copper salts prepared were the anhydrous salt and the monohydrate, and the equilibrium of both of these with their solutions was worked out. While

ammonium sulphide and potassium ferrocyanide precipitate copper from the solutions of the double carbonate, and potassium cyanide decolorizes the solution, potassium iodide has no effect upon it, and from its electrolytic behavior it appears that it is dissociated into potassium cations and $Cu(CO_3)_2$ anions, and the latter are further somewhat dissociated into copper cations and carbonate anions. From a cobalt solution treated with potassium carbonate the potassium cobaltocarbonate crystallizes out as the normal tetrahydrate. The cobalt solution is similar to that of copper but more stable. On heating it is blue but on cooling becomes a deep red-violet as at first. The $Co(CO_3)_2$ ion thus seems to be red, which is perhaps noteworthy, since some of the blue cobalt solutions are attributed to the presence of the $CoCl_4$ ions, which also contain quadrivalent cobalt.

For the investigation of fused silicates there are decided disadvantages connected with the use of platinum vessels, but Tammann has suggested the use of test tubes of carbon, rendered non-absorbent by an especially dense layer on the surface. These can be heated in the electric furnace easily as high as 2100°, and permit the study of fusions of silica with various oxides to be carried out with great facility. Using these tubes, Stein (*Z. anorg. Chem.*, **55**, 159) has investigated the preparation of a large number of silicates, formed by fusing the oxides together. He also finds that pure silica, which is viscous at 1600°, becomes at 1750° thin fluid, and sublimes. The sublimate, which forms several rings, is tridymite above, and just below a broad ring of vitreous silica. Even by slow cooling the fused silica could not be made to crystallize. Heating quartz revealed by discontinuous expansion the existence of a transition point at 552°, while chalcedony showed one at 173° and flint none between 100° and 600°.

An easy preparation of titanium tetrachloride has been described by Ellis (*Chem. News*, **95**, 122). Rutile is easily powdered after having been heated to 1000° and chilled in water. The powder is then mixed with half its weight of aluminum powder in a Hessian crucible at 500°, and the mixture ignited by burning magnesium. The product is broken up when cold and heated to a red heat in a current of dry chlorine. Titanium tetrachloride distils over and can be separated from the silicon tetrachloride formed at the same time by fractional distillation. The fact that some of the latter product is formed shows that free silicon must have been formed in the reaction with the aluminum, but inasmuch as silica is with difficulty reduced by aluminum alone, the cause of the reduction must be the great heat generated in the reduction of the titanium oxide by the aluminum.

An important piece of work is being carried out by Rosenheim in going over the chemistry of zirconium to see how much of the work of the past can stand, in the advances of inorganic chemistry of recent years. It is needless to say, that here, as practically everywhere else that this test is applied to inorganic chemistry, much of the earlier work becomes null and void. Rosenheim's second and third papers (*Ber.*, **40**, 803, 810) deal with salts of some of the more common acids. Two strong tendencies appear in zirconium salts, which have been long recognized, *viz.*, the formation of basic (zirconyl) salts, and the formation of complex acid-zirconates, in which the zirconium is in the anion. The former

tendency is illustrated by the great difficulty of preparing normal zirconium salts. Even from a concentrated hydrochloric acid solution the zirconyl chloride and not the zirconium tetrachloride crystallizes out, and the presence of hydrobromic or nitric acid does not overcome the hydrolytic tendency. By evaporating a solution with excess of nitric acid at 15° over phosphorus pentoxide the hydrated normal nitrate is obtained, but even here there appears to be considerable ground for supposing that the compound is really a complex zirconyl-nitric acid (nitrato-zirconic acid), $H_2ZrO(NO_3)_4.4H_2O$. The normal zirconium acetate may be prepared by the action of anhydrous acetic acid on the anhydrous chloride. Quite a series of new compounds have been prepared by Rosenheim by this reaction with the anhydrous zirconium chloride and organic acids, aldehydes and esters. In general, two of the chlorine atoms of the chloride are replaced, and if any moisture is present, these two atoms are replaced by oxygen by hydrolysis. The compounds with salicylic ester and aldehyde, $ZrCl_2(O.C_6H_4.CO_2CH_3)_2$ and $ZrCl_2(O.C_6H_4.CHO)_2$, will serve as examples of these compounds. The zirconium tetracetate undergoes partial hydrolysis in the presence of moisture, forming zirconyl acetate, but in aqueous solution is rapidly and completely hydrolyzed; indeed, this is suggested as an excellent method of preparing a solution of colloidal zirconium hydroxide. The normal sulphato-zirconic acid, $H_4Zr(SO_4)_4$, has not been prepared by Rosenheim, nor by Hauser, who has been studying the sulphates of this metal chiefly from the standpoint of physical chemistry (*Z. anorg. Chem.*, **54**, 196); but the potassium salt of this acid has been long known (so-called double sulphate of zirconium and potassium), and Rosenheim prepared the analogous sodium salt. The ordinary 'zirconyl sulphuric acid' has the formula $H_2ZrO(SO_4)_2.3H_2O$, or possibly $H_2Zr(OH)_2(SO_4)_2.2H_2O$. In more concentrated sulphuric acid solutions Hauser obtained an 'acid sulphate' of the formula $Zr(SO_4)_2.H_2SO_4.3H_2O$, which should more probably be considered as one-fourth hydrolyzed normal sulphato-zirconic acid, $H_3Zr(OH)(SO_4)_3.2H_2O$. The corresponding oxalic acid compound, $H_3Zr(OH)(C_2O_4)_3.7H_2O$, was prepared by Rosenheim, as well as the potassium salt of the normal oxalo-zirconic acid, $K_4Zr(C_2O_4)_4.5H_2O$, and the half hydrolyzed acid, $H_2ZrO(C_2O_4)_2.3H_2O$. The latter is the ordinary zirconyl oxalate. The only salt of a complex tartrate that was obtained was the potassium salt of the half hydrolyzed tartrato-zirconate, $K_2ZrO(C_4H_4O_6)_2.3H_2O$. Hauser (*Ibid.*, **53**, 74), by heating the sulphate, which had been previously dried at 400°, in a current of hydrogen sulphide at a moderate red heat, obtained an oxysulphide, ZrOS. If this is exposed to the air before it has become completely cold, it ignites spontaneously. The oxysulphide of thorium was obtained in a similar way and was somewhat more stable. Matignon (*Ann. chim. phys.* (8), **10**, 130) finds that thorium dioxide is slowly converted into thorium tetrachloride by heating in a porcelain tube in a current of dry carbonyl chloride, but the conversion is more satisfactorily brought about by heating in a current of carbon tetrachloride at a temperature not quite high enough to sublime the thorium chloride. If the operation is interrupted before the oxide is converted completely into the chloride, and the product rubbed up with absolute alcohol, the crystallized oxychloride, $ThOCl_2$, is obtained, which is insoluble in alcohol but soluble in water. Pure metallic

thorium cannot be prepared by the action of sodium on the chloride, as the oxide will always be present. The hydride of thorium dissociates very easily, its dissociation pressure reaching 760 mm. below 400°. It is, however, not immediately acted on by chlorine at ordinary temperature. Attention should also be called to a paper by Schenck and Rassbach (*Ber.*, **40**, 2185) on the chemical equilibria between lead sulphide and its oxidation products. It does not admit of brief abstraction but is an example of the application of the study of conditions of equilibrium to an important metallurgical problem.

Group V.—But three or four papers have appeared the past year on the combustion of nitrogen in the electric flame, and these do not indicate much progress in the study of the reaction, although it is claimed that considerable advances have been made from a practical standpoint. When one takes into account the enormous industrial importance and possibilities connected with the manufacture of nitric acid and nitrates from the air, and on the other hand the great differences in output with the slightest variations in conditions, it will be realized that few processes offer more opportunities for investigation.

An interesting addition to the compounds of nitrogen is that of monochloramine, NH_2Cl, which has been prepared by Raschig (*Chem.-Ztg.*, **31**, 926). Starting with the well-known blue coloration produced when aniline is oxidized in aqueous solution by hypochlorites and the fact that no color is produced if the hypochlorite has been previously treated with ammonia, Raschig found that when one molecule of ammonia is added to one molecule of sodium hypochlorite, monochloramine and sodium hydroxide are formed quantitatively. The solution can be distilled in a vacuum at low temperature and a pure solution of the new compound obtained, indeed, by using concentrated solutions and a high vacuum it was found possible to obtain it in pale yellow, oily drops, floating on the distillate. Monochloramine is very volatile, with a very irritating odor, resembling that of nitrogen chloride, and is very unstable. With potassium iodide it reacts giving a dark brown solution of what is possibly moniodamine, but which soon decomposes into ordinary iodide of nitrogen. The chloramine reacts with ammonia, with the production of either nitrogen or hydrazine, according to circumstances. Traces of iron, cobalt and other metals act as catalytic agents accelerating the decomposition into nitrogen, especially in the presence of substances, such as acetone, which decrease the viscosity of the solution. On the other hand, boiling the solution, especially in the presence of such substances as increase the viscosity, and of an excess of ammonia, tends to promote the formation of hydrazine. By the use of albumen, casein and gelatin it was found possible to obtain from 60–80 per cent. of the theoretical yield of hydrazine, and the possibility is suggested of using the method in the commercial production of hydrazine.

By dissolving nitric anhydride in freshly distilled sulphuric anhydride, Pictet and Karl (*Compt. rend.*, **145**, 238) obtain a product which distils at about 218° and solidifies to a hard, white crystalline mass which melts at 124°. The same compound is formed by mixing solutions of each anhydride in carbon tetrachloride. The substance has the formula $(SO_3)_4N_2O_5$, and seems to be anhydride of nitric and tetrasulphuric acids. It is very hygroscopic and dissolves in water with the regeneration of the two acids.

It has a powerful action on most organic substances, frequently both nitrating and sulphonating them, while if warmed both oxidation and carbonization may take place. No satisfactory solvent for the anhydride has been found. Potassium pernitrate, KNO_4, has been prepared by Alvarez (*Chem. News*, **94**, 269; from *Ann. chim. anal. appl.*, **11**, 401) by the action of sodium peroxide upon an alcoholic solution of potassium nitrate at a low temperature. On evaporating the solution the pernitrate is obtained in good crystals, which are neutral in reaction and give characteristic, but very unstable precipitates with solutions of metallic salts. The pernitrates of the alkaline earths are white crystalline precipitates. In a similar manner Alvarez has prepared perphosphates, perarsenates and pertungstates, $NaPO_4$, $NaAsO_4$ and $NaWO_4$. The pernitrate is recommended as a powerful oxidizing agent for combustions, and it is suggested that the perphosphates can perhaps be used in medicine. An interesting series of double compounds with nitrogen sulphide has been prepared by Davis (*J. Chem. Soc.*, **89**, 1575) by direct addition in chloroform solution. $SnCl_4.2N_4S_4$, $SbCl_5.N_4S_4$ and $MoCl_5.N_4S_4$ were thus prepared. Tungsten hexachloride and titanium tetrachloride were both first reduced and then gave the compounds $WCl_4.N_4S_4$ and $2TiCl_3.N_4S_4$. No compounds could be obtained with ferric chloride or the trichlorides of antimony and arsenic. All of the addition products were very unstable in moist air.

A useful lecture experiment to show the conversion of yellow into red phosphorus and at the same time illustrate the action of a catalytic agent is described by Zecchini (*Gaz. chim. ital.*, **37**, i, 422). Into a glass tube 30 cm. long and 7 or 8 mm. diameter and closed at one end, is put sufficient dry yellow phosphorus to fill the tube one-third full when melted. The tube is then heated to about 180° in a concentrated sulphuric acid bath. A fragment of iodine is then dropped onto the surface of the fused phosphorus, and the conversion of the yellow phosphorus into the red proceeds rapidly. According to Wolter (*Chem.-Ztg.*, **31**, 640) when phosphorus 'sesquisulphide,' P_4S_3, is shaken with a solution of iodine in carbon bisulphide, the color of the iodine disappears, and becomes golden yellow, and on cooling or on the addition of a little benzene or petroleum ether, characteristic orange leaflets of the di-iodide, $P_4S_3I_2$, are formed. Since none of the other sulphides of phosphorus give characteristic compounds with iodine, this reaction can serve to detect the presence of the 'sesquisulphide' in matches and other easily inflammable masses.

A number of salts of sulphato-arsenious acids have been prepared by Kühl (*Arch. der Pharm.*, **245**, 377), by heating together arsenious oxide and a sulphate in concentrated sulphuric acid solution, and evaporating off the acid. These salts are all somewhat basic, if one may use that term toward the arsenious acid, but should perhaps be better called oxy-salts. Such are $K_4As_2O(SO_4)_4$, $CaAs_2O(SO_4)_3$ and $PbAs_2O_2(SO_4)_2$. Somewhat similar salts of antimony (*Z. anorg. Chem.*, **54**, 256) are derived from a meta-sulphato-antimonious acid, as $AgSb(SO_4)_2$ and $Ca(Sb(SO_4)_2)_2.6H_2O$. Corresponding salts of tin, prepared by Weinland and Kühl (*Ibid.*, 244) are derived generally from the meta-sulphato-stannic acid, as $K_2Sn(SO_4)_3$ and $CaSn(SO_4)_3.3H_2O$. Some are, however, derived from the ortho-acid, as $ThSn(SO_4)_4.2H_2O$ and $CeHSn(SO_4)_4$. The titanium

salts (*Ibid.*, 253) are derived generally from meta-sulphato-titanic acid, as $CaTi(SO_4)_3$. With molybdic acid also double sulphates are formed (*Ibid.*, 259), one type being a pyro-sulphato-molybdate, $K_2Mo_2O_4(SO_4)_3.6H_2O$, and another having only one oxygen of a pyromolybdate replaced by the sulphate group, as $K_2Mo_2O_6(SO_4).6H_2O$. All of these compounds are looked upon by Weinland and Kühl as being arsenites, antimonites, stannates, titanates and molybdates, in which the oxygen atoms are more or less completely replaced by sulphate groups.

In quite an extended study of vanadium, Rutter (*Ibid.*, **52**, 368) has prepared salts of bivalent vanadium by the electrolytic reduction of vanadic acid in the presence of sulphur dioxide, using a tile diaphragm and mercury cathode with low temperature. While it was not possible to prepare crystals of vanadous sulphate, crystals of the double ammonium sulphate were easily obtained, $(NH_4)_2V(SO_4)_2.6H_2O$. Vanadous sulphate oxidizes so readily that in the absence of oxygen a dilute solution decomposes with evolution of hydrogen, while if the solution is concentrated hydrogen sulphide is given off. When solutions of bivalent vanadium are mixed with vanadium solutions of other valences, equilibria are at once attained. Bivalent and quadrivalent give trivalent vanadium as a green solution, while vanadic acid with bivalent vanadium gives first a quadrivalent and then a trivalent solution. A study of the accelerating action of vanadium pentoxide on oxidation processes has been made by Naumann and his pupils (*Jour. pr. Chem.* [2], **75**, 146). Small traces of the pentoxide accelerate very markedly the oxidation of sugar to oxalic acid by nitric acid, and the reaction can be easily studied by precipitating the oxalic acid formed and titrating with permanganate solution. If the temperature is allowed to reach 70°, the oxalic acid is further oxidized to carbon dioxide. When a mixture of air and alcohol vapor is led over a layer of asbestos which has been saturated with vanadium pentoxide, the alcohol is oxidized to aldehyde with some acetic acid, while the vanadium asbestos becomes red-hot. The oxidation of stannous salts to stannic by nitric acid or by potassium chlorate and hydrochloric acid is greatly accelerated by the presence of vanadic acid, but on the other hand, the oxidation of ferrous and manganous salts seems scarcely affected. The accelerating action of vanadium pentoxide is attributed by Naumann to the readiness with which it gives up one atom of oxygen, becoming the tetroxide, which in turn is quickly re-oxidized by whatever oxidizing agent happens to be present. Thus if to a slightly warmed, acid solution of the pentoxide is added a sugar solution, the blue color of the tetroxide at once appears, only to give place to the yellow color of the pentoxide as soon as a few drops of nitric acid are added.

The interest connected with the use of tantalum in the incandescent light has naturally begun to stir up chemists to the further investigation of this puzzling element and its neighbor, columbium. While no inconsiderable number of chemists have worked with these metals, it is probably true that less is known of their chemistry than of any other two elements, if we except those that show radioactivity. Werner von Bolton (*Z. Elektrochem.*, **13**, 145) has, probably for the first time, prepared pure columbium, previous workers apparently having had in their hands only a lower oxide or a carbide. Bolton mixes columbium pentoxide with paraffin and makes it into fibers that are reduced to the tetroxide

by heating in charcoal powder. The tetroxide as thus obtained is a conductor and is reduced to the metal by heating highly with the alternating current in a vacuum. If the direct current is used, only a lower oxide is obtained, which is, however, a good conductor of electricity. Columbium was also prepared by the Goldschmidt reaction. It is a bright light gray metal, unacted upon by acids. It is about as hard as wrought iron, malleable and ductile, and can be welded at a red heat. It is so passive as an anode that it may find industrial application. Although it fuses only at 1950°, it 'dusts' so badly at high temperatures that its use in incandescent lights is precluded. When heated in hydrogen the hydride, CbH, is formed, which is readily oxidized, while the metal itself is only slowly acted on by oxygen at even a red heat. With nitrogen it forms a nitride. At a red heat in chlorine the pentachloride is produced, and it is also attacked by fused alkalies, by sulphur and selenium. It forms no amalgam with mercury but alloys with iron in all proportions. The chlor- and bromcolumbates and tantalates have been studied by Weinland (*Z. anorg. Chem.*, **54**, 223) and for the most part are formed according to the type M'_2CbOCl_5 (or $CbOCl_3.2M'Cl$). The chlorcolumbates of the alkalies crystallize in octahedra, seemingly belonging to the type of chlorplatinates in which one atom of chlorine is replaced by one atom of oxygen. Weinland has also found (*Ber.*, **39**, 4042) that the oxychloride of 'quinquivalent chromium' prepared by him last year, forms double salts with the alkali chlorides, having the formula $M_2'CrOCl_5$ ($CrOCl_3.2M'Cl$). These crystals also have the octahedral habit, although only the caesium and rubidium salts belong to the regular system. A similar case is that of the monoxychlorosmates discovered by Wintrebert, and another the dioxychlorruthenates and dioxychlorosmates. With organic bases other types of chlorcolumbates appear, but all are compounds of the oxychloride, $CbOCl_3$, and the same is true regarding the chlorotantalates. The bichloride of tantalum has been prepared as a dihydrate, $TaCl_2.2H_2O$, by Chabrié (*Compt. rend.*, **144**, 804) by the reduction of the pentachloride with sodium amalgam at a red heat, and crystallization from concentrated hydrochloric acid in a vacuum. The green color of this chloride is seen when tantalum solutions are reduced by various agents, but it very readily becomes oxidized. The properties of both these metals have also been examined by Muthmann (*Ann.*, **355**, 58), with essentially the same results as found by von Bolton. A moderate red heat is required to oxidize columbium, the tetroxide, Cb_2O_4, being formed, while tantalum burns at a lower temperature to the pentoxide, Ta_2O_5.

Group VI.—In a recent paper (*Z. anorg. Chem.*, **56**, 233) Marino argues in favor of a new class of dioxides. When manganese dioxide is treated with sulphur dioxide, manganese dithionate is the principal product, though there is some sulphite formed. With lead dioxide, sulphur dioxide gives at first lead sulphite and oxygen, which latter immediately oxidizes the sulphurous acid to sulphuric. The course of the reactions, as followed by Marino, is:

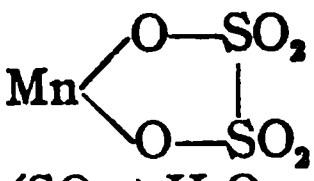
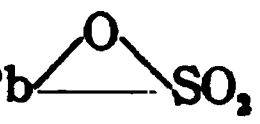
$$\text{I. } PbO_2 + SO_2 = PbSO_3 + O$$
$$\text{II. } SO_2 + O + H_2O = H_2SO_4$$
$$\text{III. } PbSO_3 + H_2SO_4 = PbSO_4 + H_2SO_3.$$

With true peroxides, the reaction is:

$$\text{I. } BaO_2 + H_2SO_3 = BaSO_3 + H_2O_2$$
$$\text{II. } SO_2 + H_2O_2 = H_2SO_4$$
$$\text{III. } BaSO_3 + H_2O_2 = BaSO_4 + H_2O.$$

In neither of these cases is any trace of dithionate formed. From the reactions with hydrochloric acid, it may be assumed that in lead and manganese dioxide the oxygen is united solely to the metal and that the metal is quadrivalent, while in barium dioxide the barium is bivalent and the atoms of oxygen are united together, as shown by the hydrogen peroxide formation. From the dithionate reaction it is probable that the formula of manganese dioxide is $Mn\begin{matrix}O\\O\end{matrix}$, but from the fact that lead dioxide forms only the sulphite, it must have some other formula. The only two which conform to the conditions are $Pb\begin{matrix}O\\|\\O\end{matrix}$ and $Pb\begin{matrix}O\\\|\\O\end{matrix}$. The former of these is the more probable since the sulphite formed from it has the asymmetrical formula, as was experimentally shown by its reaction with dimethyl sulphate. Its reaction with sulphur dioxide is then $Pb\begin{matrix}O\\|\\O\end{matrix} + SO_2 = Pb\begin{matrix}SO_2\\|\\O\end{matrix} + O$. Lead dioxide may thus be considered to belong to a hitherto undescribed type of dioxides. Since the formation of a dithionate is conditioned upon the group $\overset{IV}{M}\begin{matrix}O\\O\end{matrix}$, and since a dithionate is formed when sulphur dioxide reacts with the sesquioxides of iron, cobalt and nickel, it follows that the constitution of these sesquioxides is not, as generally assumed, $\begin{matrix}M=O\\ \diagdown O\\ M=O\end{matrix}$ or $\begin{matrix}M=O\\ |\diagdown O\\ M=O\end{matrix}$, but $O=M=M\begin{matrix}O\\O\end{matrix}$. In the opinion of the reviewer the conclusions of Marino do not seem to be well justified. Aside from the question as to whether there is any real difference between the two constitutions $M\begin{matrix}O\\O\end{matrix}$ and $M\begin{matrix}O\\|\\O\end{matrix}$ (which is extremely doubtful), the constitution proposed for the sesquioxides is improbable. There is no other evidence to indicate that all of the metal in these compounds is not uniformly trivalent (or $[M_2]^{VI}$). Further, the fact that MnO_2 gives dithionate, and PbO_2 primarily sulphite, does not necessitate a difference in constitution of the dioxides. The difference in solubility of lead and manganese compounds is quite sufficient to account for the breaking down of the primarily formed quadrivalent sulphites along different lines. The primary reaction would be $\overset{IV}{M}\begin{matrix}O\\O\end{matrix} + 2SO_2 = M\begin{matrix}O\\O\end{matrix}\begin{matrix}SO_2\\SO_2\end{matrix}$

In the case of manganese the reduction in valence of the metal is to


and in the case of lead to the insoluble  and $(SO_3+H_2O=)H_2SO_4$, as found by Marino.

The old problem of the constitution of the thiosulphates has been attacked by Julius Meyer (*Ber.*, **40**, 1351) from the standpoint of the double thiosulphates, but no very definite results have been obtained. The double thiosulphates are in general quite unstable, but a pretty full series of the lead, silver and copper thiosulphates with the alkalies was prepared. $Cs_2S_2O_3.PbS_2O_3.2H_2O$ is a salt of a type which frequently occurs, though quite a number of other types exist, sometimes more than one with the same two metals, as for example the rubidium-copper thiosulphates, of which three distinct salts were prepared. In the case of some of the ammoniacal double thiosulphates of silver both white and yellow salts were obtained, which Meyer thinks may possibly point to a difference in constitution, the silver in the one case being attached to oxygen and in the other to sulphur. The difference in color may, however, be due to other causes, as the salts have not the same formula. In the case of the double rubidium salts, the white salt is $Rb_2S_2O_3.Ag_2S_2O_3.NH_3$, and the yellow salt $3Rb_2S_2O_3.4Ag_2S_2O_3.NH_3$.

In reviewing the sixth group, the work of Norris, published in THIS JOURNAL (**28**, 1675), on the elementary nature of tellurium should not be passed over. There seems to be little doubt but that tellurium is rightly placed as a member of the sixth group of the periodic system, but the most careful determinations of its atomic weight agree in placing it above iodine. Mendeléeff and others have plausibly conjectured that the discrepancies are due to the presence of some element, such as Mendeléeff's dvitellurium, in our ordinary tellurium, and special efforts have been made by several chemists to separate out such an element. In earlier work with Fay and Edgerly, Norris purified potassium bromotellurate by fractional crystallization, Brauner sublimed the tetrabromide of tellurium, and Köthner distilled tellurium itself fractionally. Since the boiling points of both the bromides of selenium and tellurium, and of the elements themselves, are not far apart, it is probable that a higher element of the same group would not differ greatly in its own boiling-point or in that of its bromide. Consequently it might be difficult to separate such an element if it were present in tellurium. On the other hand, there is a great difference between the boiling points of the dioxides of sulphur, selenium and tellurium, and it is probable that the dioxide of a heavier element of the sulphur group could be readily separated from the other members by sublimation. Norris therefore purified tellurium by the sublimation of the dioxide, but no difference in the atomic weights of the different fractions could be detected. In order to purify tellurium from any element of any other group, the reaction of sodium thiosulphate with tellurium dioxide to form the tellurium analogue of the pentathionate, $Na_2S_4TeO_6$, was utilized. This breaks up by alkalies into the tetrathionate and tellurium. It is hardly possible that any element of another group could replace sulphur in the pentathionate, so the precipitated tellurium from this compound may be considered free from any element except sulphur (and possibly selenium). On further purification this tellurium shows the same atomic weight as that purified in other ways.

This work of Norris's presents further strong confirmation of the elementary nature of what we now know as tellurium, and the solution of the problem of its anomalous position in the periodic table must be sought in some other direction. A paper has just appeared by Marckwald (*Ber.*, **40**, 4730) on the atomic weight of tellurium which seems to bring out a new phase of the subject. Marckwald admits that the work of Norris and others has conclusively demonstrated the absence of any other element in their tellurium, which could affect its atomic weight, but he claims that most of the atomic weight determinations thus far made are defective. He has carried out a number of determinations based on heating H_6TeO_6 and weighing the TeO_2 formed, and gets fairly concordant results, with an average of 126.85 ± 0.02. As this is below the accepted atomic weight of iodine, it puts a new face on the whole matter, and the criticisms and results of the other workers in this field may prove interesting.

In the light of Werner's theory of the constitution of inorganic compounds, the question of the constitution of the product formed when chromium chloride is dissolved in pyridine and the solution precipitated by water, is of interest. The product has the empiric formula, $CrCl_3(Pyr)_3$. According to Werner's theory none of the chlorine atoms should be ionizable, but the insolubility of the compound in water precludes the possibility of determining this directly. Pfeiffer (*Z. anorg. Chem.*, **55**, 97) finds that the compound can be easily dissolved in concentrated nitric acid to a deep green solution, from which water precipitates the original compound in crystalline form. From this he argues that the chlorine cannot be ionizable, since if it were, some of the chlorine would be replaced by the nitrate group. Furthermore, the compound, while insoluble in water, is soluble in pyridine, chloroform, methyl alcohol and other organic solvents, which renders it probable that it has nothing of the character of a salt. The compound must hence be looked on as the coördinated group $\left(Cr\begin{matrix}Cl_3\\Pyr_3\end{matrix}\right)$. Several papers have appeared during the year on the conditions which pertain in solutions of chromates and bichromates, but the problem still seems far from a final solution, and must be passed over here. Gröger has continued to work upon the double chromates (*Ibid.*, **51**, 348; **54**, 185), and finds that two quite general types of double chromates prevail. The type which is found in most of the double alkali sulphates of the bivalent metals, $M'_2M''(SO_4)_2.6H_2O$, is also found among the chromates, but hardly with the same frequency. It is found, for example, in the double alkali chromates of nickel and cobalt. On the other hand, a commoner type is $M'_2M''(CrO_4)_2.2H_2O$. This is found not only in the double chromates of cadmium, zinc and magnesium with potassium, but also in the potassium calcium chromate. Other types are also found, the double chromates of lead and univalent mercury with potassium being anhydrous. The large number of complex molybdates prepared by Hall have already been described in THIS JOURNAL (**29**, 692). Rosenheim has confirmed the formula of the potassium molybdi-octacyanide ($K_4Mo(CN)_8.2H_2O$) described by Chilesotti. It appears from titration experiments with potassium permanganate that this peculiar compound is a derivative of quinquivalent molybdenum. This only serves to increase the anomalous character of this

salt, which represents the unique case of a stable anion, soluble in water, which contains eight coördinated groups about one atom. Quite a number of salts of this anion were prepared by Rosenheim, and they are comparable in stability with the ferrocyanides. A quite complete investigation of the compounds of quadrivalent uranium has been published by Colani (*Ann. chim. phys.* [8], **12**, 59). The anhydrous chloride was prepared by the action of chlorine and chloride of sulphur on the dioxide, the product containing other chlorides if any other oxides are present. The tetrabromide was readily formed but the anhydrous tetraiodide could not be prepared. The sulphide, selenide, nitride, phosphide and arsenide were all found to be normal in their formulas. A large series of phosphates and double phosphates was prepared, the latter giving generally rather simple types.

Group VII.—During the past year considerable work has been published from the University of Danzig by Ruff and his pupils on fluorine and its compounds (*Ber.*, **39**, 4310; **40**, 2926; *Z. anorg. Chem.*, **52**, 256; *Z. angew. Chem.*, **20**, 1217). The pentafluoride of antimony was prepared by the action anhydrous hydrogen fluoride upon antimony pentachloride at zero, the temperature being gradually raised and the hydrogen chloride and hydrogen fluoride being successively distilled off. It was not found possible to prepare the pentafluoride by the action of hydrofluoric acid upon antimony pentoxide. With a small quantity of water the pentafluoride forms a dihydrate, but dissolves in more water to a stable solution, in which no precipitate is formed in the cold with either hydrogen sulphide or potassium iodide. While dry metals have little action upon the pentafluoride, several of the elements form addition products. Such are SbF_5I, $(SbF_5)_2I$ and SbF_5S. At about 250° an equilibrium seems to be attained with a formula $(SbF_5)_{1.4}I$, and this whether the mixture heated contained an excess of the pentafluoride or of iodine. With liquid ammonia a compound is formed with the formula $(SbF_4)_2(NH_3)_3$, which according to Ruff is probably a difluohydrate of diaminodiantimonotrifluoramide, which may be formulated $HF.NH_2.SbF_3.NH.SbF_3.NH_2.HF$. With tungsten hexachloride, tungsten hexafluoride is formed, but a better method of preparing the latter is the action of anhydrous hydrogen fluoride upon tungsten hexachloride. Arsenic trifluoride can also be used. Tungsten hexafluoride is the first fluoride of a metal which is a gas at ordinary temperature. At 19.5° it is condensed to a liquid which freezes at 2.5°. It fumes strongly in the air and is very sensitive to moisture. The oxytetrafluoride, WOF_4 was prepared, and a mixture containing this and the dioxydifluoride, WO_2F_2, but the latter could not be obtained pure. While efforts to prepare the hexachloride of molybdenum have not proved successful, and the hexafluoride could not be obtained by the action of hydrogen fluoride or any of the other fluorides, in some cases fluorine compounds of hexavalent molybdenum were obtained, but they were generally the oxytetrafluoride or the dioxydifluoride, corresponding to the tungsten oxyfluorides mentioned above. The molybdenum hexafluoride was finally prepared by the direct action of fluorine upon metallic molybdenum, obtained by the Goldschmidt process. MoF_6 fuses at 17° and boils at 35° and is a very reactive substance. Another interesting compound prepared by Ruff is the acid potassium compound of lead tetrafluoride, $PbF_4.3KF.HF$. This may also be looked

upon as the tripotassium salt of fluo-orthoplumbic acid, K_3HPbF_8. This is readily prepared in quantity and when heated gives off a part of its fluorine, hence it is proposed by Brauner to use it in the preparation of fluorine. It is probably the most stable known halide compound of quadrivalent lead. Bismuth pentafluoride was also prepared, hydrofluoric acid being used to dissolve the product obtained by the action of chlorine upon an alkaline suspension of bismuth. Lebeau has also been engaged in work upon fluorine and has prepared (*Compt. rend.*, **144**, 1042, 1347; **145**, 190) selenium tetrafluoride by the direct action of fluorine upon selenium. It boils somewhat above 100°. With an excess of fluorine no higher fluoride could be obtained. This is, however, contrary to the work of Prideaux, who obtained a hexafluoride, the vapor density of which, as determined by Ramsay, corresponded to the hexafluoride. In his later papers Lebeau seems to admit the formation of the hexafluoride. The subject of the basicity of hydrofluoric acid has been further studied by Kremann (*Monatsh.*, **28**, 917) and Pellini and Pegoraro (*Z. Elektrochem.*, **13**, 621). The former studied the conductivity of the solutions, using as a vessel a hollow block of paraffin. On the basis of Ostwald's dilution law, the acid has the formula H_2F_2. Pellini studied the conductivity on neutralizing hydrofluoric acid with alkalies, and from this concludes that the acid acts as if it were bibasic and consisted of a combination of two monobasic acids, one of which is strong and the other weak. The free acid and the neutral salts thus act as binary electrolytes, while the hydrogen fluorides and the neutralization phenomena correspond to a bibasic acid.

Recent work by Schwarz (*Z. angew. Chem.*, **20**, 138) on bleaching powder confirms the hypothesis that the underlying reaction of its formation is $Cl_2 + HOH \rightleftarrows HCl + HOCl$. This explains why the presence of water is necessary to the reaction. So long as the lime is present in excess the reaction is merely a neutralization of the acids according to the above equation. As soon, however, as the lime has all been used up, the excess of hydrochloric acid liberates hypochlorous acid from the bleaching powder and this, with the hypochlorous acid formed in the above reaction, oxidizes undecomposed hypochlorite to chlorate. The excess of chloride which is always found in commercial bleaching powder may be due, according to Schwarz, to the loss of oxygen from the hypochlorite, or to hydrochloric acid present in the chlorine used. If the amount of water present in making bleaching powder is too great, the same effect is produced as with an excess of chlorine, since the hypochlorite is very easily hydrolyzed. The fact that the synthetic bleaching powder (prepared by the action of chlorine monoxide on calcium oxide in the presence of moisture) gives up much less chlorine when treated with carbon dioxide, is probably to be explained by considering it merely a mixture of calcium chloride and calcium hypochlorite, while that prepared in the ordinary commercial method is a true double salt, $CaCl(OCl)$. Bleaching powder from strontia resembles very closely in preparation and properties, that from lime. Two new salts of some little interest are hydrazine chlorate and perchlorate, prepared by Salvadori (*Gaz. chim. ital.*, **37**, ii, 32) by the neutralization of a solution of hydrazine hydroxide with the free acids, and evaporation in a vacuum. The chlorate is exceedingly hygroscopic and has three times as great explosive force as fulminate of mercury.

Alcohol is rapidly oxidized by its solution even in the cold to aldehyde and acetic acid. Hydrazine perchlorate is, on the other hand, far more stable and can be fused at 131° on platinum foil, and burned quietly at a higher temperature. It is, however, exploded by a blow. It can be boiled in solution, even in the presence of alcohol, without decomposition. A specimen of the perchlorate was preserved for two years unchanged over calcium chloride.

Several years ago the method of preparing anhydrous chlorides by heating the oxides in a current of chlorine and chloride of sulphur was introduced. Bourion (*Compt. rend.*, **145**, 243) now finds that this reaction is equally applicable to the preparation of bromides, and he has obtained a number of new bromides of the metals by heating their oxides in a current of bromine containing a small amount of the chloride of sulphur. The amount of the latter reagent necessary for good results varies in different cases.

A new suggestion regarding the place of manganese in the periodic table has been made by Reynolds (*Chem News*, **96**, 260). Recognizing the slight resemblance between manganese and the other elements of the seventh group and the fact that no other elements of higher atomic weight have been found to take the vacant places in the second series of group seven, he transfers manganese to the first period of the eighth group, making this series, Mn, Ru, Os. The second series becomes Fe, Rh, Ir, and the third series, Ni, Pd, Pt. One advantage of this arrangement is that nickel precedes cobalt in position as it should with its undoubtedly lower atomic weight. It may be questioned, however, whether this arrangement has actually come as near the natural arrangement as the ordinary table. Cobalt would here stand alone as a single member of a fourth series of group eight. It is true that group seven with only one series would correspond to the so-called group zero with the inert gases, which has only one series, but as a matter of fact the halogen group seven corresponds rather to the alkali group one, and the compounds of manganese are no more unlike those of the halogens than are those of copper, silver and gold unlike the alkalies. According to Reynolds's arrangement, the iron-platinum metal group represents a transition from the sixth group to the first, while the inert gases would be the transition from group seven to group one. If the iron-platinum metals and the inert gases represent the two divergent series of group eight, then the iron-platinum metals are a natural transition from the positive series of group seven to the negative series of group one, while the inert gases form the transition from the negative series of the seventh group to the positive series of group one. Mention ought to be made here of the fact that Holmes (THIS JOURNAL, **29**, 1277) has succeeded in preparing the long sought for tetrachloride of manganese, by the action of dry hydrogen chloride upon freshly precipitated manganese dioxide, suspended in carbon tetrachloride. It is hydrolyzed in the presence of even a trace of water and loses chlorine on heating. This work of Holmes renders probable what has long been surmised, that the first product of the action of hydrochloric acid on manganese dioxide is the tetrachloride, and the reason that this has eluded so many investigators is not so much the inherent instability of quadrivalent manganese compounds (a thing in

itself improbable) as the great tendency of the compounds of quadrivalent manganese to hydrolyze.

Group VIII.—That in the action of iron on water the temperature and the surface are the two determining factors has of course long been recognized, but few have realized how extensive the influence of increasing the surface by using finely divided iron might become. Birnie (*Chem. Weekbl.*, 4, 291) has studied this reaction using *ferrum reductum* and the vapor of water at different temperatures. When 10–20 grams of this iron are heated in a current of steam with an ordinary gas jet, 100 cc. of hydrogen can be collected in a few moments. It is even possible to obtain a rapid evolution of hydrogen by the use of 'florists' wire,' if a sufficiently high heat is used. At a temperature of 15° with 500 grams of *ferrum reductum* little hydrogen was obtained the first day, but after that from 100–500 cc. every 24 hours. A decided evolution of hydrogen is apparent when two kilos of florists' wire is boiled with distilled water. The color of iron alum (and incidentally of other ferric salts) has long been an unsolved puzzle. It has been described as colorless, as yellow, as violet, as blue, but it has often been conjectured that the ordinary amethyst color is due to manganese, since the salts of trivalent manganese vary from amethyst to red according to concentration. Christensen (*Danske Vid. Selsk. Förh.*, 1906, 4, 173) has experimented with the fractional crystallization of iron alum and of pure iron alum to which a trace of manganic sulphate (manganic acetate in sulphuric acid) has been added. It was found that crystals could be obtained varying from colorless to garnet red, depending on the content of manganese. In the more deeply colored crystals, it is safe to say mixed alum crystals are present, but in those which are amethyst the color is possibly due to a ferric-manganic sulphate, such as has been prepared by Étard. While this salt is green, its addition to a colorless iron ammonium alum gave violet crystals. Pure iron alum is colorless but colorless iron alum is not necessarily pure, for on fractioning such an alum a mother-liquor was obtained from which violet crystals were obtained. Bellucci and his pupils have continued the work (*Atti accad. Lincei, Roma* (5), 15, ii, 467; 16, i, 654) begun several years ago on the nitrososulphides of iron (nitroprussides). By action upon the sodium salt, $NaFe_4(NO)_7S_3.2H_2O$, with the hydrochloride of hydrazine in slight excess, the hydrazine nitroprusside was obtained. The hydroxylamine salt was similarly formed but required rather longer heating to complete the reaction. The potassium, thallium, rubidium and caesium salts were readily formed by treating the hydrazine salt with the corresponding chloride, and the salts obtained in this way were all anhydrous, while when otherwise prepared they are hydrated. Nitroprussides were also prepared of a number of organic bases, such as phenylhydrazine, pyridine, tetra-alkyl ammoniums, phenylenediamine and semicarbazine. Cobalt hexamine (luteo salt) also forms a crystalline compound.

An article has lately appeared by Gross (*Elektrochem. Z.*, 14, 146) claiming the decomposition of platinum by the alternating current. Potassium carbonate was heated to a yellow heat in a platinum crucible and subjected for several hours to an alternating current of 120 volts and 35 amperes, with 50 alternations per second. A small amount of potassium nitrate was added to the melt. The platinum was strongly attacked

and in and over the melt graphite-like crystals were formed. After treatment with water a brown substance remained which was soluble in water but after heating to a red heat could be dissolved only in aqua regia. Its solution gave a dark brown precipitate with hydrogen sulphide. On evaporation of the filtrate from the melt a red-powder was obtained which was free from platinum but on solution in hydrochloric acid showed the same properties as the brown substance. The above-mentioned needles, on solution in aqua regia showed also similar properties. The total amount of new substance was 15 per cent. less than the loss of the platinum crucible and the electrodes. Gross considers that the red powder is a hydrate and the brown material the new substance itself, obtained by the decomposition of platinum. The same results were obtained when potassium hydroxide or a mixture of nitric and sulphuric acids was used as an electrolyte. Further information is to be looked for, as the data given are insufficient to form a conjecture as to the meaning of the published results, and especially as to whether the other metals which are present in all commercial platinum may not be responsible for the results obtained by Gross.

Gutbier has continued his work upon the halopalladites and palladates of organic bases as well as the pallado-amines of the same bases (*Ber.*, **39**, 4134). Pyridine, picoline, quinoline and a number of primary alkylamines were used and the results obtained are similar to those which have been previously described. The halopalladites are formed by direct union of the components in hydrochloric acid solution and can generally be recrystallized from hydrochloric acid, but on treatment with water they are decomposed with the formation of the palladamines. Gutbier has also (*Ibid.*, **40**, 690) prepared a large number of hexachlor- and bromruthenates of organic bases. His method is to saturate a solution of ruthenium trichloride with the halogen and then add the solution of the hydrochloride of the base, or to mix the trichloride with the base and then saturate the solution with chlorine or bromine. Since earlier investigations have shown that the true trichloride or rather pentachlorruthenic acid, H_2RuCl_5, and its salts are not converted into the hexachlorides directly by the addition of chlorine, but only after they have been converted into the aquochlorides, it must have been the latter, $M'_2Ru(H_2O)Cl_5$, with which Gutbier worked. The acid solution of the trichloride is readily converted into the aquochloride by heating its solution with alcohol and other organic substances, so that this change may well have occurred in the presence of the organic substances with which Gutbier was working. The properties of Gutbier's hexahaloruthenates agree with those of the corresponding hexahaloruthenates of the alkali metals. A very useful piece of work has been carried on by Paal and Amberger (*Ibid.*, **40**, 1378) on the quantitative determination of osmium. When a compound of osmium can be heated in a hydrogen current and reduced to the metal, this can be very satisfactorily handled on a Gooch filter, as has been well worked out by Wintrebert; but where the osmium is in solution the problem is difficult. Paal and Amberger have gone critically over the whole ground of the quantitative precipitation of osmium, testing no less than ten proposed methods, generally with very unsatisfactory results. When the osmium is in the form of osmium tetroxide ('osmic acid') it can be completely precipitated by alcohol on long standing,

though the precipitate is a hydrogel and hard to wash. Other compounds of osmium, as the osmates, are also precipitated by alcohol but here again the precipitate is difficult to free from alkalies, if they are present. No method, which can be considered thoroughly satisfactory, is known by which osmium can be quantitatively precipitated. The same is even more true of ruthenium, for no method is yet known by which this metal can be completely precipitated from solution.

WASHINGTON & LEE UNIVERSITY,
LEXINGTON, VA.
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ON THE NON-EQUIVALENCE OF THE FOUR VALENCES OF THE CARBON ATOM.[1]

BY J. U. NEF.

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Three assumptions are made with reference to the carbon atom in our present system of organic chemistry: first, that the valence of this atom is invariably four; second, that the four valences are equivalent; and third, that they are distributed in three dimensions and act in the direction of the axes of a tetrahedron.

If we believe, as many at present are inclined to do, that the chemical forces are analogous to or identical with the electrical forms of energy, it at once becomes improbable that the four valences of the carbon atom can be equivalent. Had Berzelius, for example, realized that the molecules of hydrogen and oxygen were each composed of two atoms he would have developed his electrochemical theory from a different standpoint; he would have concluded, as have Clausius, Schönbein, and many others in more recent times, that the forces holding the two atoms of oxygen or hydrogen together in these molecules must be alternately positive and negative.

Let us first analyze critically, however, the evidence which has led us, for some fifty years past, to assume that the four valences of a carbon atom are equivalent. In the last analysis the fact that up to the present moment every one of the great number of monosubstitution products of methane has been found to exist in one modification only is all we have to justify our assumption. There is but one acetic acid, one nitromethane, one aniline, one acetaldehyde, etc., etc. It is evident that we are here drawing positive conclusions from negative evidence—always an unreliable and dangerous process of reasoning. How can we ever be certain when we have a monosubstitution product before us that it is not always one and the same hydrogen atom of marsh gas which has been replaced?

A Belgian chemist, Henry,[2] has spent a number of years in trying to prove by experiment that any one of the four hydrogen atoms of methane, *a*, *b*, *c* or *d*, may be replaced by the carboxyl or nitro group and yet give thus one and the same acetic acid or nitromethane respectively. Such experiments can not conceivably be decisive, for they necessitate the unjustifiable assumption that the various atoms or radicals bound to the

[1] See THIS JOURNAL, 26, 1549–1577. Read at the Chicago meeting of the American Chemical Society.

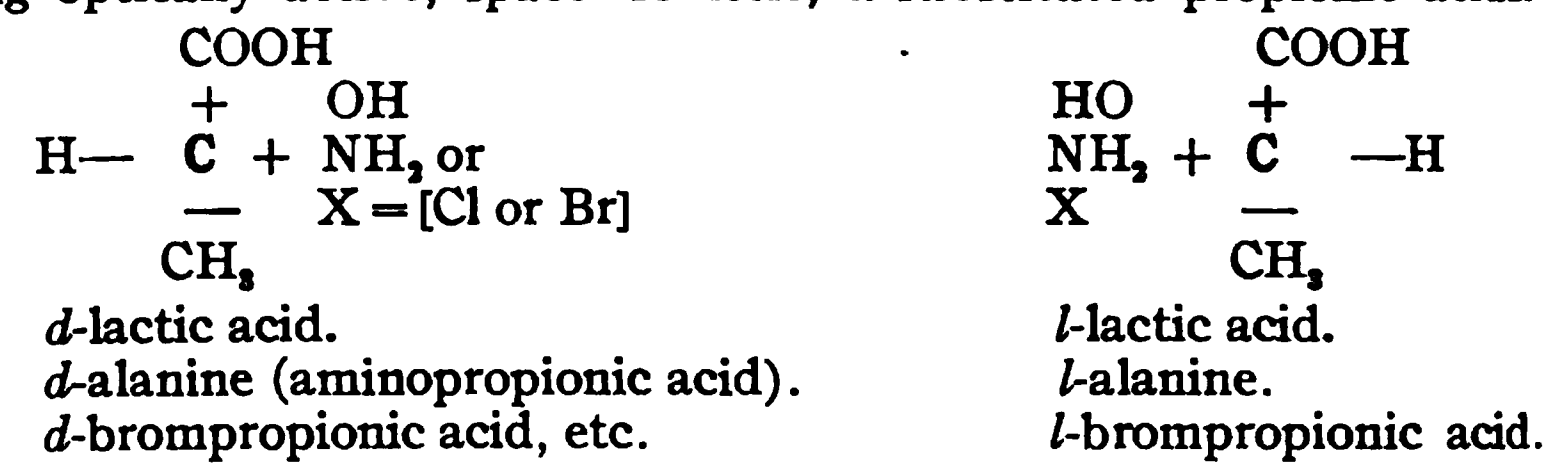
[2] Bull. acad. royal de Belgique (3), 12, 644; 15, 333.

four different valences of a carbon atom hold their places. A study of the optically active α-brompropionic acids, the brom-phenylacetic and succinic acids (see below) shows for instance very decisively that such an interchange of radicals is continually taking place at ordinary temperature.

The present situation with reference to the nature of the four valences of the carbon atom may therefore very properly be summed up in the following words; we assume their equivalence until there is proof to the contrary.

During the past ten years or more there has accumulated quite a mass of evidence pointing unquestionably to the conclusion that the four affinity units of carbon are equivalent in pairs only, as shown by the following expression, $^{+}_{-}{}^{-}_{-}C^{-}_{-}{}^{-}_{+}$, in which the plus and minus signs do not necessarily mean positively and negatively charged valences, but are simply used to discriminate between two different kinds of affinity units.

Allow me to call your attention to certain reactions shown by the following optically active, space isomeric, α-substituted propionic acids.



d-lactic acid. *l*-lactic acid.
d-alanine (aminopropionic acid). *l*-alanine.
d-brompropionic acid, etc. *l*-brompropionic acid.

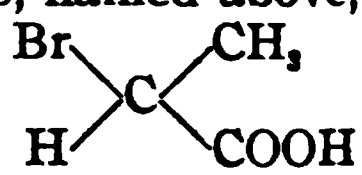
When *d*- or *l*-brompropionic acid, or its ester, is treated with ammonia we always obtain the *corresponding*, optically active, α-amino acid, *d*- or *l*-alanine, or its ester. Similarly when these same brom acid esters are treated with various metallic hydroxides, the *corresponding*, optically active, *d*- or *l*-lactic acid derivatives are obtained.

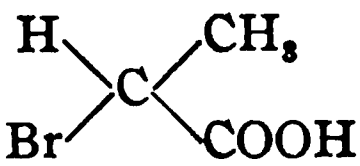
During the past twelve years an enormous amount of evidence has accumulated which shows that the interaction of the primary and secondary alkyl halides, RCH_2X and R_2CHX, with ammonia, metallic hydroxides, or with silver salts of various acids proceeds through the following successive stages:

(*a*) $R_2CHX \rightleftarrows R_2C{<} + HX + 2NH_3 \rightarrow R_2C\begin{cases} H \\ NH_2 \end{cases} + NH_4X.$

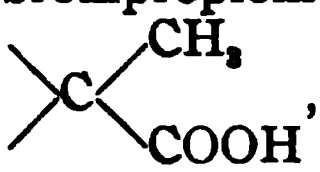
(*b*) $R_2CHX \rightleftarrows R_2C{<} + H{-}X + M{-}OH \rightarrow$
$R_2C{<} + MX + H{-}OH \rightarrow R_2CHOH + MX.$

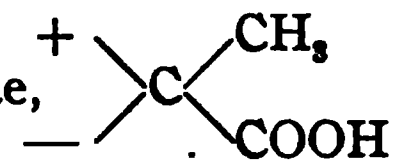
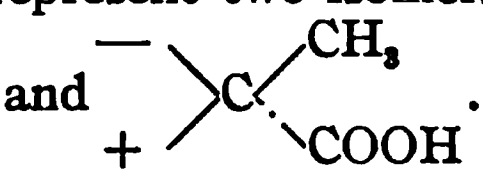
(*c*) $R_2CHX \rightleftarrows R_2C{<} + H{-}X + Ag{-}A \rightarrow$
$R_2C{<} + AgX + H{-}A \rightarrow R_2CHA + AgX.$

Now the two space isomeric α-brompropionic acids, named above, may be regarded as α-carboxylated ethyl bromides, 

and 

; they must therefore be entirely analogous in their reactions to the secondary alkyl bromides. It is furthermore evident at a glance that if the four valences of carbon were equivalent both *d*-

and *l*-brompropionic acid must give by loss of hydrogen bromide, HBr +  , through dissociation, one and the same ethylidene carboxylic acid; this substance must theno bviously absorb ammonia, H—NH_2, water, H—OH, or the acid H—A, to give equal amounts of both *dextro*- and *laevo*-alanine or lactic acid derivatives respectively.

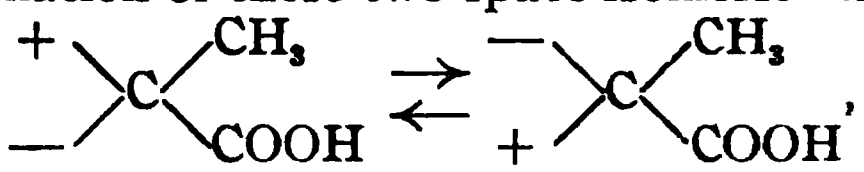
This can, however, *not* be the result provided the two valences of carbon in ethylidene carboxylic acid are unlike; the two methylene derivatives obtained from *d*- and *l*-brompropionic acid by loss of hydrogen bromide must then in fact not be identical but represent two isomers of space as shown by the formulae,  and  . These substances then obviously absorb the dissociated ammonia, H—NH_2, or water, H—OH, present to give *d*- or *l*-alanine or the corresponding *d*- or *l*-lactic acid derivative—which agrees with the facts.[1] The moment, therefore, we admit the correctness of the interpretation given of the action of alkyl halides with ammonia, water, etc., the facts presented above prove with precision that two of the four valences of carbon can not be equivalent.

This conclusion also enables us to comprehend in a more simple manner the phenomenon of autoracemation, and especially to understand why optically active substances can maintain their independent existence notwithstanding the fact that the various groups or radicals bound to the different valences of carbon are also continually dissociated from them; thus *d*- or *l*-lactic acid, *d*- or *l*-alanine, *d*- or *l*-brompropionic acid although partially dissociated at ordinary temperatures into *d*- or *l*-ethylidene carboxylic acid and water, ammonia or hydrogen bromide respectively, maintain their identity for a long period of time. Nevertheless the optically active brompropionic acids, as well as their esters, and the corresponding monobromsuccinic and phenylacetic acid derivatives go over-as Walden has shown,[2] on long standing (two to five years) at ordinary temperatures into a mixture of equal amounts of the *d*- and *l*-compounds. *Dextro* and *laevo* lactic acid, on the other hand, can be kept indefinitely without change at ordinary temperatures and yet each changes very quickly, in two to three days, at 140° into racemic, *i. e.*, *d-l*-lactic acid.

The analogous *d*- and *l*-iodopropionic acids are as yet unknown, but it is certain that they must transform themselves with great speed at ordinary temperatures into racemates so that their actual isolation is problematical. Why are there these remarkable differences in the stability of quite analogous optically active compounds? It is due simply to a difference in the relative amount of existing dissociation. The alkyl iodides are relatively far more dissociated into $C_n H_{2n}$ and HI than the

[1] I am purposely avoiding here a discussion of the remarkable optical inversion observed by Walden [(*Ber.*, 32, 1833-55) and by Fischer (*Ibid.*, 40, 489)] in a few isolated instances in the malic and lactic acid series—a reaction which all admit is abnormal and one which, in my opinion, when better understood, will also lead to the conclusion that the four valences of carbon are not equivalent.

[2] *Ber.*, 31, 1420.

corresponding bromides, chlorides or fluorides—hence the well-known far greater activity of the alkyliodides, alkylsulphates, etc. Furthermore it is obvious in the case of the α-substituted propionic acids under discussion, that as soon as the percentage of dissociation in these compounds into *d*- and *l*-ethylidenecarboxylic acid reaches a certain definite limit, then a very slow transformation of these two space isomeric methylene derivatives into each other,  , must automatically take place—hence the phenomenon of autoracemation.

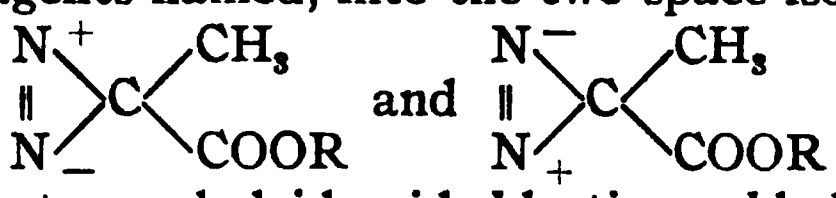
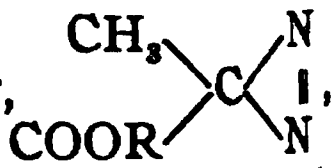
Finally, and this is important, since the above interpretation of the reactions of the alkyl halides is not yet generally accepted by chemists, we may reach the same conclusion, namely, that the four valences of carbon are not equivalent, from an entirely different standpoint by considering another series of reactions shown also at ordinary temperatures by optically active amino acids. When *d*- or *l*-alanine ester is treated with nitrous acid, nitrosyl bromide or chloride respectively we always obtain the *corresponding*, optically active *d*- or *l*-lactic, brom- or chlorpropionic ester. Now the well-known conversion of primary amines into alcohols or alkyl halides by means of nitrous acid or nitrosyl halide has been shown to proceed, in the aliphatic series, through the following stages, *a* or *b*:

$$(a)\ HO{-}N{=}O + H{-}NHC_nH_{2n+1} \rightarrow HO{-}N\langle^{OH}_{NHC_nH_{2n+1}} \rightarrow$$

$$C_nH_{2n}\langle^{N}_{\|}_{N} + 2H_2O \rightarrow C_nH_{2n+1}OH + N_2 + H_2O.$$

$$(b)\ X{-}N{=}O + H{-}NHC_nH_{2n+1} \rightarrow X{-}N\langle^{OH}_{NHC_nH_{2n+1}} \rightarrow$$

$$C_nH_{2n}\langle^{N}_{\|}_{N} + H_2O + HX \rightarrow C_nH_{2n+1}X + N_2 + H_2O.$$

i. e., through an intermediate formation of a fatty diazo compound. Consequently *d*- as well as *l*-alanine ester must go over, when treated with the reagents named, into the two space isomeric *d*- and *l*-α-diazopropionic esters,  ; the first of these must give with water or haloid acid *d*-lactic or *d*-halogenpropionic acid, whereas the second one is necessarily converted, with evolution of nitrogen, into the corresponding antipodes. It is of course at once apparent that if the two valences of carbon bound to nitrogen in diazopropionic ester,  , were equivalent, both *d*- and *l*-alanine must give on treatment with nitrous acid or nitrosyl halide respectively equal amounts of the *d*- and *l*-derivatives, *i. e.*, racemates or at any rate the same products—which is however not the case; consequently the two diazopropionic esters which

are the intermediate products[1] in the various reactions are not identical but isomers of space—in other words the two valences of carbon joined to nitrogen in these compounds are *not* equivalent.

Have we any other evidence which throws doubt on the equivalence of the four valences of carbon? Yes. I refer to asymmetric addition, which shows us in a most simple manner why we have such a vast array of optically active substances in the vegetable and animal kingdom. You are all familiar with the properties of the unsaturated hydrocarbons called the olefines; they absorb with great ease, by addition, such substances as hydrogen, halogens, sulphuric acid and haloid acids. Now propylene absorbs the two last-named reagents to give almost exclusively the isopropyl derivatives,

$$\begin{array}{l} CH_3CH{-}CH_2 \\ \quad\;\; | \qquad\;\; | \\ HOSO_2{-}O \quad H \end{array} \quad \text{and} \quad \begin{array}{l} CH_3CH{-}CH_2 \\ \quad\;\; | \qquad\;\; | \\ \quad\;\; X \qquad\;\; H \end{array}. \quad \text{Why is this?}$$

The absorption reaction takes place first because we have in propylene a certain very definite but small number of molecules in an active molecular condition, thus,

$$\underset{\text{Inert propylene.}}{CH_3CH{=}CH_2} \rightleftarrows \underset{\text{Active propylene.}}{CH_3CH{-}CH_2}$$

Furthermore the concentrated sulphuric acid or the dry haloid acid is also partially dissociated into the active masses, H— and —OSO_2OH or —X respectively. Hence a simple union takes place between these active substances to give the addition products named above.

Now if we assume the equivalence of the four valences of carbon it is very difficult to understand why the addition of the dissociated H and X particles does not take place equally on both active carbon atoms of propylene giving like amounts of the propyl and isopropyl derivatives, $CH_3\underset{X}{CH}{-}\underset{H}{CH_2}$ and $CH_3\underset{H}{CH}{-}\underset{X}{CH_2}$, respectively. This is self-evident when we realize that the two active valences of active propylene are not equivalent but must be represented thus:

$$CH_3CH \overset{+\;-}{\underset{-\;+}{=}} CH_2 \rightleftarrows CH_3\underset{-}{CH}{-}\underset{+}{CH_2}(I) \text{ and } CH_3\underset{+}{CH}{-}\underset{-}{CH_2}(II).$$

We have now only to make the further assumption that active propylene contains at ordinary temperatures relatively more active (II) than active (I) molecules; the addition of the dissociated reagent, $\overset{+}{H}{-}\overset{-}{X}$, must then obviously give $CH_3\underset{X}{CH}{-}\underset{H}{CH_2}$ as the chief product.

[1] In view of the importance of ascertaining this with certainty, I am at present working on the problem of isolating these two isomers of space. It is obvious, as Dr. A. F. McLeod suggested to me in reading this paper, that the long known space isomerism existing among the oximes of ketones and aldehydes, as well as among the diazo and azo compounds, may likewise be due to the non-equivalence of the valences of the carbon and nitrogen atoms respectively.

Emil Fischer's work in the sugar group shows that prussic acid when added to various aldoses often gives a decided preponderance of one of the two isomers theoretically possible. Similarly the benzilic acid rearrangement, which also depends upon an addition of active carbon monoxide to various aldoses,[1] often proceeds asymmetrically.

We are thus able to understand, in a strikingly simple way, why various enzymes can convert the sugars into optically active destruction products such as *d*- or *l*-lactic acid, etc., etc. Finally we may ask ourselves whether the two unlike valences of carbon are positively and negatively charged. It is impossible to answer this question with certainty at the present time; it is my conviction, however, that the peculiar ease with which carbon forms chains of great complexity and stability, as well as the fact that the vast majority of the carbon compounds are non-ionizable substances whose reactions proceed mainly in the manner indicated above,[2] must be attributed to the non-equivalence of the four valences of the carbon atom; furthermore the existence of various compounds containing bivalent carbon can also be readily understood on this basis.

NEW BOOKS.

Immunochemistry. The Application of the Principles of Physical Chemistry to the Study of the Biological Antibodies. By SVANTE ARRHENIUS. The Macmillan Company. Price, $1.60.

The preface of this book states that the contents contain a summary of six lectures on the immunity reactions, delivered at the University of California during the summer of 1904, amplified by the addition of new matter covering the subject to the date of publication. No information is given as to whether this is a translation of the German edition, or conversely; but as the German edition preceded the American by several months the latter is presumably a translation, which assumption is supported by the occasional occurrence of characteristic German forms of construction.

Under the title of "Immuno-chemistry" (a useful term which this book will probably cause to be adopted into the vocabulary of the "immunologist") Arrhenius gathers much of the literature bearing upon the studies that have so far been made of the chemical nature of the reactions of immunity, but most of the space is devoted to discussion and interpretation of the results so far obtained by the application of the methods of physical chemistry to the problems of immunity. As by far the greater part of this work has been done by, or under the direction of the author or his colleague, Dr. Madsen, the "Immuno-chemistry" partakes largely of the nature of a monograph upon the physical chemistry of immunity reactions; consequently a review of the book almost necessarily resolves itself into a criticism of the value of the in-

[1] Cf. *Ann.*, 357, 231–3.

[2] See THIS JOURNAL, 26, 1577.

vestigations upon the physical chemistry of the immunity reactions that are therein recorded. Certainly when a physical chemist of the pre-eminent standing of Prof. Arrhenius collaborates with so experienced an investigator of the problems of immunity as Prof. Madsen, the outcome of their labors is sure to receive most respectful consideration, and whether one does or does not agree with all their conclusions, none will deny that they have opened an almost untouched field of research to general investigation. The results and hypotheses produced by their work and recorded in collected form in this book are certain to stimulate a great amount of research and controversy, which are bound to be fruitful whether or not they confirm the conclusions of Arrhenius; therefore the actual value of this book is certain to be very great, and it constitutes a welcome addition to the literature of immunity. As to the actual significance of the results so far obtained through the study of immunity reactions by the methods of physical chemistry, there is room for difference of opinion. Already many of the conclusions expressed in this book, and previously published in special periodicals, have been sharply attacked; and in the opinion of the reviewer these attacks have been justified, for there is no question that among the many investigations recorded are to be found serious errors of experiment and of interpretation. To discuss the specific points of Arrhenius's work that have been found open to attack would require more space than can well be allotted to a book review, but it may be stated that the chief source of error would seem to lie in the enormous disparity that exists between the very exact *methods* of physical chemistry and the very uncertain *materials* of immunology, which makes the application of one to the other a very hazardous procedure.

Only the investigations of numerous workers through a long period of time can finally decide the actual value of the work done and the conclusions reached by Arrhenius and Madsen and their adherents, but whether supported or not, its stimulating influence is certain to have a profound effect upon the future development of our knowledge of this all-important subject of immunity. As the authorized exposition of this work, Arrhenius's "Immuno-chemistry" will of necessity stand as a classic in the literature of immunity, and to pick at the faults of style and rhetoric would be trivial; to attempt to judge its actual present worth or to predict future valuation would be presumptuous. Its usefulness is assured, and it will be read eagerly, and *very* critically, by every student and investigator of the processes of immunity. It is unfortunate that the exigencies of the subject are such that the book will be read understandingly by but a very limited number of scientists; the unavoidable use of the complicated terminology of immunity will stand in the way of the chemist, except in those sections devoted to the

physical chemistry of enzyme reactions, where there is gathered much valuable material; on the other hand, the constant and necessary use of mathematical expression will be a serious obstacle, unfortunately, to many immunologists. H. GIDEON WELLS.

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SOLUTION OF METALS IN NON-METALLIC SOLVENTS; II.[1] ON THE FORMATION OF COMPOUNDS BETWEEN METALS AND AMMONIA.

BY CHARLES A. KRAUS.

Received February 14, 1908.

Solutions of metals in liquid ammonia were first obtained by Weyl,[2] who brought together sodium and potassium with gaseous ammonia under pressure. However, he mistook the solutions which are formed under these conditions for simple compounds and assigned to them the formulae $NaNH_3$ and KNH_3, respectively. These compounds he supposed to be structurally analogous to the hypothetical free ammonium group, being derived therefrom by substitution of an atom of hydrogen by one of the metal in question. Taking account of this relationship in his nomenclature, he introduced the terms sodammonium and potassammonium, respectively, which nomenclature has been largely adopted by subsequent investigators and commentators.

The study of solutions of metals in ammonia was materially advanced by Seely,[3] who showed conclusively that solutions result in the action of ammonia on the alkali metals. From a consideration of the optical properties of these solutions, he concluded that a compound was not formed between the two components. Neither Weyl nor Seely, however, was able to adduce quantitative data in support of his contention.

These investigations on the action of ammonia on the alkali metals

[1] For the first paper of this series, "I. General Properties of Solutions of Metals in Liquid Ammonia," see THIS JOURNAL, 29, 1557–1571 (1907).

[2] *Ann. Physik*, 121, 601 (1864).

[3] *Chem. News*, 23, 169 (1871).

seem to have excited little active interest for, excepting an isolated observation by Gore,[1] we find no further investigations recorded until 1889, when Joannis[2] undertook an extended series of investigations in this field. To him belongs the credit of bringing quantitative data to bear on the problem of the compounds formed by sodium and potassium with ammonia. He devised a means of isolating and analyzing these compounds, to which he assigned the composition $NaNH_3$ and KNH_3 respectively, and to which, like Weyl, he ascribed an ammonium structure. Employing the method devised by Joannis, Moissan obtained the compounds $LiNH_3$, $Ca(NH_3)_4$[3] and $LiCH_3NH_2$,[4] while Mentrel obtained the compound $Ba(NH_3)_6$[5] and Roederer the compound $Sr(NH_3)_6$.[6]

In the preceding paper[7] attention was called to the fact that the concentrated solutions of metals in ammonia exhibit metallic reflection and are consequently opaque. It is plain, therefore, that the formation of a compound cannot be ascertained by visual observations nor can separation of the different phases in these concentrated solutions be carried out by the simple means usually employed in the preparation of a pure substance. The method adopted by Joannis in preparing and identifying the compounds in question is therefore an indirect one, as will be seen from the description given below. Objections have been raised from time to time to the results obtained by Joannis as well as to those obtained by other chemists employing the same method.

It is the purpose of the present paper to determine, if possible, whether or not compounds are formed. To this end I shall first examine such evidence as is already at hand. The solutions of sodium and potassium in ammonia have been studied extensively and, as will be seen below, the available data are sufficient to enable us to draw the conclusion that solid compounds are not formed. In the case of other metals it has been found necessary to adduce new experimental evidence. It will thus be shown that lithium, like sodium and potassium, does not form a solid compound, while calcium forms the compound $Ca(NH_3)_6$ with ammonia. Finally the questions of constitution and nomenclature will be considered and the physical properties of the compound $Ca(NH_3)_6$ will be discussed briefly.

Criterion for the Appearance of New Phases.

In determining whether compounds are formed between a solvent and a dissolved substance, it is of primary importance to possess a clear

[1] *Phil. Mag.*, **44**, 315 (1873).
[2] *Compt. rend.*, **109**, 900 (1889).
[3] *Ibid.*, **127**, 685 (1898).
[4] *Ibid.*, **128**, 26 (1899).
[5] *Ibid.*, **135**, 790 (1902); *Bull. soc. chim.*, **29**, 493 (1903).
[6] *Compt. rend.*, **140**, 1252 (1905).
[7] THIS JOURNAL, **29**, 1570.

knowledge of the phase relations before attempting to identify any of these phases as compounds by means of chemical analysis. Since the solutions of metals in ammonia constitute two component systems, it follows that if ammonia is withdrawn from the system, the pressure must become constant as soon as a third phase appears. If, on continuing the withdrawal of ammonia, one phase disappears the pressure will again vary when ammonia is withdrawn. If, however, one of the three phases is substituted by a new third phase, the pressure changes abruptly to a new constant value. One of the phases present is always gaseous ammonia; the other two phases may either be both solid or liquid, or one may be liqiud and the other solid. It is an easy matter to determine how many new phases make their appearance in withdrawing ammonia from a dilute solution of a metal until the free metal and gaseous ammonia are left behind. The study of the vapor pressure of a system of metal and ammonia is therefore a necessary preliminary in determining whether compounds are formed. The nature of the phases present at any time may, in general, at once be determined by visual-examination, and by proper means it is always possible to transform the entire system into any desired phase, when its composition may be determined by analysis.

Non-existence of the Compounds $NaNH_3$ and KNH_3.

The pressure of the systems sodium-ammonia and potassium-ammonia have been carefully investigated by Joannis.[1] He finds that in the case of both these systems, if ammonia is withdrawn from a solution of the metal, the vapor pressure falls until a solid phase makes its appearance, after which the pressure of the system remains constant until only free metal and gaseous ammonia are left. This would seem to show that the solid phase which initially separates from solution is free metal. Joannis, however, believes that such is not the case. He observed that the solid, which initially precipitates, appears to possess the same color of metallic reflection as does the solution itself, while, as is well known, the free metal possesses white metallic reflection. He therefore considers that this solid may be a compound of sodium with ammonia. We shall simply call this substance "solid compound" in order to avoid circumlocution. This substance is evidently a new phase; the question only remains to show whether it is a compound, as Joannis believes it to be, or, otherwise, free metal and saturated solution as the vapor pressure relations indicate. According to Joannis, free metal does not make its appearance until the saturated solution is completely converted into the solid compound, after which, on further withdrawal of ammonia, the free metal appears, without being accompanied by any change in

[1] *Loc. cit.*: For details of the method described in this paragraph v. *Ann. chim. phys.*, 7, 13–36 (1906).

the pressure. He assumes, therefore, that the dissociation pressure of the "solid compound" is exactly equal to the vapor pressure of its saturated solution. Analysis of the "solid compound" gave him a composition corresponding to the simple formula $MeNH_3$, where Me may be either Na or K.

According to the phase rule, the system, vapor, saturated solution, "solid compound," and free metal must be an invariant one and obtainable at a single temperature only, since two components and four phases are present. Roozeboom[1] first called attention to these facts and suggested that Joannis had carried out his experiments at the temperature of this invariant point. Joannis, however, showed that at a series of temperatures no change occurs in the pressure from the moment that a solid phase begins to separate until only free metal and gaseous ammonia are left. This proves conclusively that the solid phase initially separating out of the solution is identical with the solid phase which is finally left behind, namely, free metal, and that a solid compound is not formed between the metal and ammonia. The "solid compound" can consist only of free metal and saturated solution of the same in ammonia. Ruff and Geisel[2] have recently expressed this view and in addition they have adduced some evidence to show that the solid compound consists of a free metal covered with a film of solution, which adheres through the action of strong surface forces. Joannis,[3] replying to this paper of Ruff and Geisel, throws some doubt on the correctness of the conclusion which they have drawn from their experimental results. In the section dealing with lithium, whose behavior is in every way similar to that of sodium and potassium, I shall adduce independent evidence showing conclusively that, in accordance with the view of Ruff and Geisel, the so-called compound $LiNH_3$ contains solution and free metal. This evidence was not obtained primarily to show that compounds do not exist, for as to this point the thermodynamic evidence would seem to be sufficient in itself. Since, however, Joannis[4] believes that his hypothesis may be reconciled with the phase rule, it may be as well to give evidence which is quite independent of any theoretical considerations.

This reconciliation of his hypothesis with the phase rule Joannis[5] believes to have been effected by Moutier.[6] A careful examination of Moutier's paper fails to show, however, that such a reconciliation is possible. A consideration of the free energy of a system can lead to no results other than those obtainable by other thermodynamic methods.

[1] *Compt. rend.*, 110, 134 (1890).
[2] *Ber.*, 39, 831 (1906).
[3] *Ann. chim. phys.*, 11, 101 (1907).
[4] *Loc. cit.*
[5] *Loc. cit.*, 103; *Ann. chim. phys.*, 7, 34 (1906).
[6] *Compt. rend.*, 110, 518 (1890).

The conclusions reached by Moutier are in fact applicable to a single temperature only and not to a series of temperatures, as be believes them to be.

Vapor Pressure of the System $LiNH_3$.

According to Moissan,[1] the compound $LiNH_3$ is formed. Since he employed the same method as did Joannis in the case of sodium and potassium and since confirmatory vapor pressure measurements were lacking, it seemed advisable to determine the pressure relations of the system $Li-NH_3$.

The apparatus employed need not be described in detail. It consisted essentially of a tube permanently attached to a manometer and containing the solution. Provisions were made for connecting this tube with a source of pure ammonia vapor or a vacuum pump as desired. After introducing the metal into the containing tube, it was placed in a bath at —10° and ammonia vapor was introduced under a pressure slightly greater than one atmosphere. The process of condensation and solution takes place with great facility in the case of lithium, even at ordinary temperatures. When the process of solution was complete the container was placed in a bath at 20° and the excess of ammonia was allowed to escape under a pressure of about 100 cm. of mercury. On withdrawing ammonia by means of the pump, the pressure fell until it reached a value of about 10 centimeters, after which it remained constant. At this point a solid phase began to separate out and on continuing the withdrawal of ammonia the amount of solid increased. The solid phase appeared to have the same color as the solution and the solution apparently disappeared long before all the ammonia had been completely withdrawn. The pressure, however, remained constant until only free metallic lithium was left behind. When but very little ammonia was present the color distributed appeared uniformly over the entire surface of metal, giving it a slight tinge of color. On adding more ammonia the color became more pronounced while, at the same time, the crystals of metal, which previously were very sharply defined, lost their sharp outline, their edges becoming indistinct. The phenomenon is such as we should expect if the crystals were covered by a film of highly colored metallic solution.

The equilibrium pressure of the saturated solution of lithium in ammonia was measured at a number of temperatures with the following results:

Temperature.	Pressure.	Mean.	Temperature.	Pressure.	Mean.
19.3°	9.48 cm. 9.58 "	9.53 cm.	9.75°	5.68 cm. 5.72 "	5.70 cm.
0°	3.31 " 3.31 "	3.31 "	20.3°	9.91 " 10.06 "	9.98 "
0°	3.31 " 3.32 "	3.31 "	20.3°	9.90 " 10.06 "	9.98 "

[1] *Compt. rend.*, **127**, 685 (1898).

The pressures first recorded were obtained after abstracting, the second after adding ammonia.

From the pressure data the heat evolved when one gram-molecule of ammonia vapor combines with metal under equilibrium conditions to form a saturated solution may be calculated from the equation:

$$Q = 4.6 \frac{T_1 T_2}{T_2 - T_1} \log. \frac{p_2}{p_1}.$$

Using the values of p at 0° and 20.3°, respectively, we thus obtain Q = 8698 calories. The value of P at 9.75° calculated from this value of Q is 5.699 cm. while the value 5.70 was found.

Independent Evidence Showing that the Solid Compound $LiNH_3$ is Not Formed.

The pressure relations recorded above show conclusively that a compound is not formed between lithium and ammonia. It seemed worth while to examine the behavior of lithium solutions somewhat further in order to determine, if possible, the sources of the error in the result of Moissan. In common with other investigators who have adopted the method of Joannis, he finds that so long as the amount of ammonia present exceeds that corresponding to the formula $LiNH_3$, that is, when saturated solution is present, any free bit of metal at once absorbs ammonia from the saturated solution to form the compound. On the other hand, when the amount of ammonia is less than that which corresponds to the formula $LiNH_3$, a free surface of metal remains permanently free from ammonia. This is, in fact, the criterion which these investigators employ in determining when the saturated solution disappears and the supposedly "solid compound" begins to dissociate. Since no change occurs in the pressure when the composition passes through the point corresponding to the composition $LiNH_3$, it is difficult to understand why there should be any difference in the behavior of the system on one side and the other of this point. The following experiments were undertaken for the purpose of obtaining more light on this question.

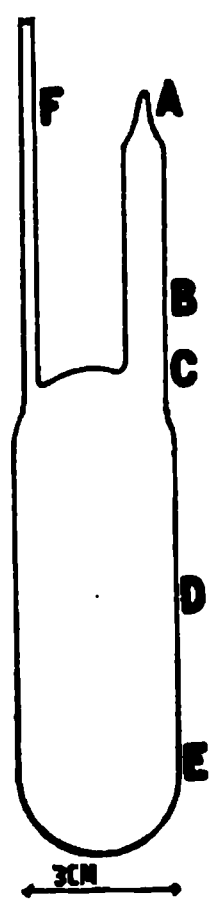

Fig. 1.—Apparatus employed in studying lithium solutions.

A quantity of lithium was introduced into a tube of the form outlined in Fig. 1. Ammonia was condensed at 0° until the metal had all dissolved, after which ammonia was withdrawn by means of the pump until a portion of the metal had been precipitated. A portion of the solution spattered along the walls of the tube EC, while a few isolated drops of solution could be seen clinging to the walls of the smaller tube AC.

On immersing the tube as far as E in a bath at 15°, 10° below room temperature, the solvent at once evapo-

rated from the isolated drops in AC, leaving metal behind, while along the walls of the tube EDC the metal retained ammonia. This portion of the tube was then warmed with the hand, whereupon the ammonia evaporated. As soon as this heating process was discontinued, the solution from the bottom could be seen creeping up over the walls of the tube. The solution passed from crystal to crystal, tracing out characteristic figures, such as would naturally result if a liquid were to creep over a surface covered with irregularly spaced particles. Isolated particles of metal like those in the tube AC underwent no change whatever. On plunging the entire tube in the bath the particles in AC remained unaffected.

After repeating the above operation a number of times, it was observed that the amount of metal in the space DC had greatly increased. This is evidently due to the fact that the metal on the walls of the tube acts as a wick by means of which solution is drawn from the colder portion of the tube in the bottom to the warmer portions above. Here the solvent evaporates to condense again in the bottom, while the metal is left behind in the warmer portion of the tube. To test this further, the tube was left immersed as far as E in a bath at 12°. At the end of 45 minutes the metal had crept up the tube AC over a distance of more than a centimeter, forming a very heavy deposit. The deposit of metal in CD had now become so heavy that it could not be freed from ammonia by warming with the hand. The tube was left immersed as far as D in a bath at 0° for some time, after which all the ammonia was withdrawn. On examination it was found that no metal was left in the bottom, it having collected in the warmer portion of the tube DC.

A small quantity of ammonia was now introduced, sufficient to form only a thin film on the surface of the metal. The tube was placed in ice-water as far as C, while the metal deposit extended about 1.5 cm. above C in AC. On warming the tube at B with the hand, the metal deposit crept up the tube with visible speed, and at the end of about ten minutes the entire surface of the tube AC was coated with metal. The tube AC was kept warm for some time, after which the ammonia was again withdrawn. Nearly all the metal now appeared collected in the tube AC.

It is remarkable that this process should take place so rapidly against a temperature difference of nearly 30°. No better illustration could be given of the strength of the surface forces coming into play between the metal and its solution. It is to be remembered that the amount of ammonia was but a small fraction of that required to form a compound of the composition $LiNH_3$. This experiment, therefore, shows conclusively that liquid is present in the system even when, according to Moissan, only the compound $LiNH_3$ should be present. These experiments show, moreover, that the behavior of the system is the same irre-

spective of the amount of ammonia present so long as this is less than that necessary to form a saturated solution of all the metal present. Those phenomena which Moissan employed in isolating the supposed compound $LiNH_3$, I have been quite unable to reproduce. It is clear, then, that in accordance with the vapor pressure relations, the properties of lithium in the presence of small quantities of ammonia, are such as to preclude the possibility of a compound being formed at the temperatures of the present experiments.

The behavior of other alkali metals is doubtless similar to that of lithium. In the case of sodium I have observed this experimentally. Caesium and rubidium have not been investigated as regards their vapor pressure relations. Moissan[1] obtained what he believed to be the compounds $CsNH_3$ and $RbNH_3$. It seems not improbable, however, that the same errors underlie the results obtained with these metals as has been shown to underlie those obtained with the remaining alkali metals.

The Vapor Pressure of the System Ca-NH_3.

It having been shown that the alkali metals do not form compounds with ammonia, it seemed important to examine at least one member of the group of the alkaline earths. For this purpose calcium was selected. According to Moissan, the compound $Ca(NH_3)_4$ is formed, the method employed being that of Joannis, which has been shown to be untrustworthy. Pressure data were not obtained by Moissan, but he states that above 0° calcium combines with ammonia without liquefaction, while at lower temperatures liquefaction takes place. This indicates that a solid compound is formed whose dissociation pressure lies below one atmosphere, while the vapor pressure of its saturated solution lies above one atmosphere at temperatures in the neighborhood of 0°. That this is correct, follows from the experiments about to be described.

Observations on the phase relations in the more dilute solutions of calcium in ammonia were made in connection with some conductivity experiments. Solutions of calcium, like those of sodium, separate into two liquid phases. The point of complete miscibility of these two phases lies at much higher temperatures in the case of calcium than it does in that of sodium. Even at room temperatures, the concentration of the two phases differs very widely. At —33° the concentration of the dilute phase does not exceed 1/10 gram-atom per liter, while that of the concentrated phase is such that pronounced metallic reflection results. Owing to the tendency of the concentrated phase to cling to the walls of the containing tube and also, perhaps, because of the small difference in the specific gravity of the two phases, it was not possible to separate them into two layers, one above the other. The fact that the concentra-

[1] *Loc. cit.*

ted solution clings to the walls of the container made it very difficult to determine the nature of the system. However, on using very large quantities of solvent and small quantities of metal the concentrated phase could be plainly seen adhering at intervals to the walls of the tube or floating about in the dilute solution.

In studying the concentrated solutions of calcium, a tube of the form outlined in Fig. 2 was employed. The tube G serves as a receptacle for the metal or its solution. At F it is joined to the manometer system C by means of a bit of rubber tubing. The stop-cocks D and E are provided so that at any time G may be detached and weighed, the cocks being closed beforehand. When G is again attached, the air is exhausted from the tube ED before opening E. The cocks A and B make connection with a source of pure ammonia and a vacuum pump, respectively.

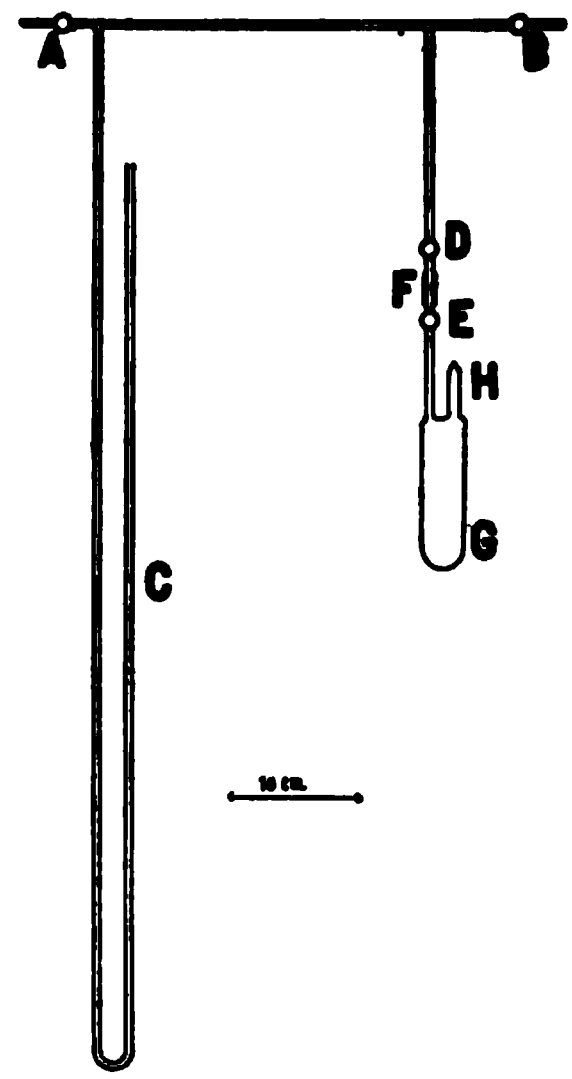

Fig. 2.—Apparatus employed in analyzing calcium compounds.

A piece of metal, freshly cleaned, is introduced into G through H, which is immediately sealed off, after which G is exhausted. The tube G having been weighed beforehand, the weight of metal is obtained by detaching G and weighing. The amount of ammonia present in G at any time may be obtained in a similar manner.

After having introduced a quantity of metal according to the method described above, G was placed in a bath at 20° and ammonia vapor was introduced under a pressure slightly greater than one atmosphere. At the end of 10 minutes appreciable absorption of ammonia had not taken place. Even at 0°, absorption was inappreciable at the end of 5 minutes. The containing tube was then placed in a bath at —33° and ammonia was condensed. It was noticeable that calcium dissolves at a much slower rate than do the alkali metals. When the metal was all in solution, the tube was allowed to warm up, the excess of ammonia being allowed to escape under a pressure of 1 1/3 atmospheres. In the neighborhood of 0°, the liquid disappeared, leaving behind what appeared to be a solid metallic substance identical in color with the solution from which it was precipitated and possessing the mechanical properties of a solid.

The tube was now placed in a bath at 22° and ammonia was withdrawn by means of the pump. The pressure fell rapidly and reached a

constant value at 10 centimeters. Pressure readings were carried out at different temperatures with the following results:

Temperature.	Pressure.
10.8°	4.60
0°	2.28
21.7°	9.07
21.7°	9.07
43.7°	30.67

The last two determinations were made at different times. The equilibrium pressure could be reached from one side only. This was due to the extreme slowness with which ammonia combines with calcium. Such combination does take place, however, as will be seen below. In the last experiment a slow increase in pressure was noted, due, without doubt, to the formation of amide and hydrogen from the two constituents.

Calculating, as above, the value of Q from the pressures at 0° and 21.7° we find Q = 10,230 calories for the heat evolved when one gram-molecule of ammonia combines with calcium to form the compound in question. This value of Q gives the pressures 4.66 cm. and 30.20 cm. at 10.8° and 43.7°, respectively. The corresponding values found are 4.60 cm. and 30.67 cm.

The tube was now cooled to —33°, and ammonia was again condensed until the metal was dissolved. Leaving the tube G in its bath of boiling ammonia, solvent was withdrawn with the pump. The pressure soon reached a constant value at about 50 centimeters and a solid substance apparently crystallized from solution. Evidently a compound precipitates out of solution at this pressure, which in turn loses ammonia at a much lower pressure.

A fresh piece of calcium weighing 0.4189 gram was introduced into G, and ammonia was condensed until the process of solution was complete. Leaving the tube in its bath, ammonia was withdrawn until the pressure became constant and solid began to precipitate. The following pressure observations were then made:

Temperature.	Pressure.	Approached from
—32.5°	47.42 cm.	higher pressure
—32.5°	46.98 "	lower "
—32.5°	47.28 "	higher "
—50°	19.28 "	higher "
—50°	19.28 "	lower "
—32.5°	47.18 "	higher "
—32.5°	47.08 "	lower "
—32.5°	47.42 "	higher "

As may be seen, the pressure reading differs slightly according as the equilibrium is approached from higher or from lower pressures. This is due to the slowness with which equilibrium establishes itself. Tak-

ing the mean of these observations, we obtain the following values for the pressure of the saturated solution, namely: $t = 50°$, $p = 19.28$ cm., $t = -32.5°$, $p = 47.18$ cm.

For the heat of solution, we obtain from these data, by calculation, the value $Q = 5458$ calories when one gram-molecule of gaseous ammonia dissolves the compound under equilibrium conditions to form a saturated solution.

The pressure-composition curve for calcium and ammonia at $-32.5°$ is represented in Fig. 3, where the ordinates represent pressures in centimeters and the abscissae composition in mols of calcium per 100 mols of calcium and ammonia. Portions of the curve are exaggerated in order to bring out certain points. The correct pressures, however, appear on the margin. Along AB we have the change in pressure of a dilute solution with concentration. At B, a second liquid phase of concentration

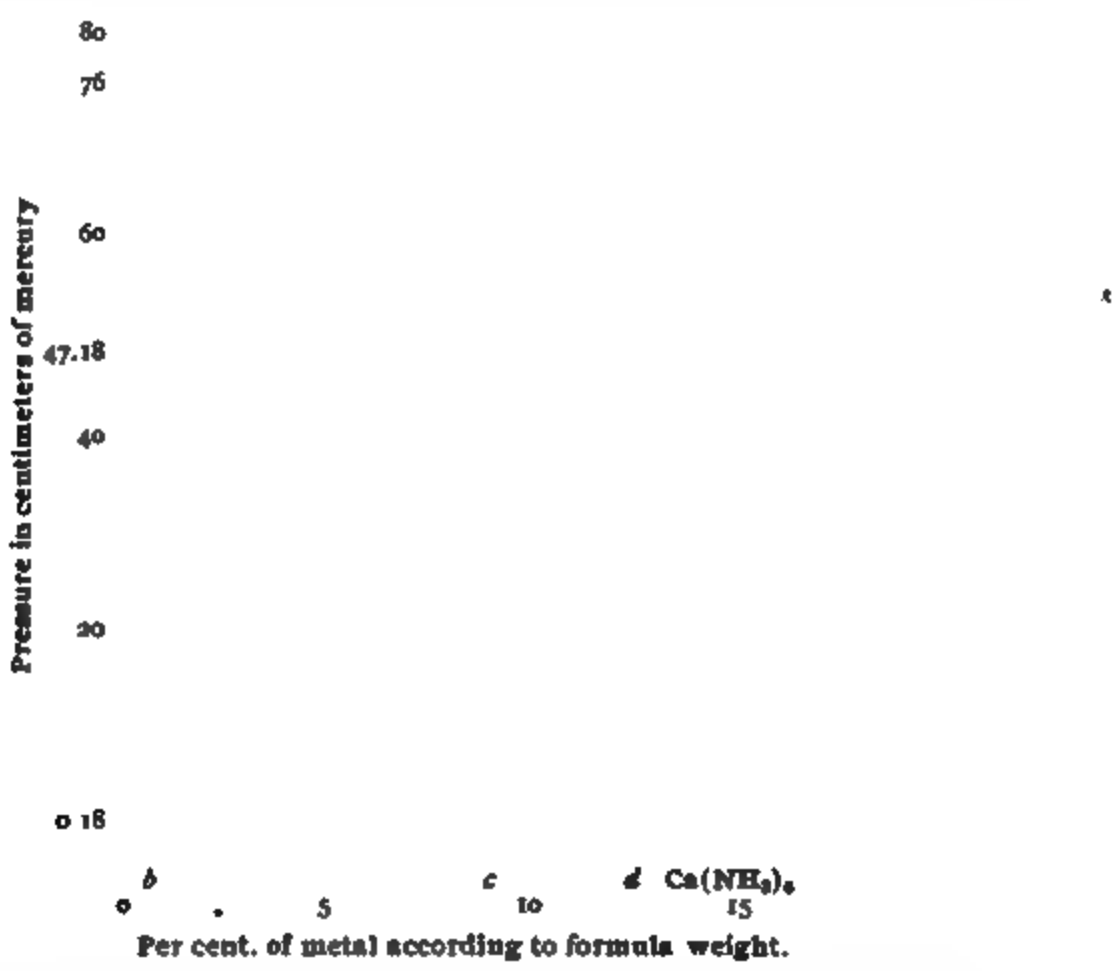

Fig. 3.—Vapor pressure—composition curve for calcium in ammonia.

c appears, and the pressure remains constant until the dilute phase of concentration b disappears. This pressure is within a millimeter of the atmospheric pressure, since b is very small. Along CD the pressure falls to 47.18 cm., when the solid compound of composition $Ca(NH_3)_6$ (see below) appears. The pressure now remains constant until the saturated solution of composition d disappears, when the pressure falls abruptly to 1.8 mm. (calculated) and metallic calcium appears. This pressure is maintained as long as the solid compound remains. That

the solid compound does not lose its ammonia in two steps instead of one was shown by measuring the pressure: first when the compound had lost but a little ammonia, and second when only a small amount of ammonia was present in the system. This result will be referred to below in connection with the possible formation of the compound $Ca(NH_3)_4$.

Moissan[1] states that calcium does not absorb ammonia above 20°. As already stated, calcium in the massive form absorbs ammonia very slowly even at 0°. This is to be expected, since a compound is formed which does not liquefy in the presence of ammonia. By employing very finely divided calcium, as it may be obtained by completely withdrawing the ammonia from a solution of the same, it was found that at temperatures above 20° ammonia combines with calcium, although the process is a very slow one.

Composition of the Compound of Calcium and Ammonia.

Experiment 1.—In the preceding experiment in which the vapor pressure of a saturated solution of the compound of calcium in ammonia was determined, 0.4198 gram of metal was employed. At the end of the pressure experiments, which occupied in all about 8 hours, the solution was placed in a bath at 0° and ammonia was withdrawn until a pressure of about 10 centimeters was reached. The tube was then weighed. The contents of the tube weighed 0.9873 gram in excess of that of the metal present. Assuming that this excess in weight is due to ammonia combined with calcium, we may calculate n the number of molecules of ammonia per atom of calcium. We thus have

$$n = \frac{0.9873 \times 40.1}{0.4198 \times 17.06} = 5.529.$$

The correct value is probably either 5 or 6. In view of the fact that the solution was prepared eight hours before analysis was made, it is not improbable that a portion of the metal reacted with the solvent according to the equation: $Ca + 2NH_3 = Ca(NH_2)_2 + H_2$.

Experiment 2.—To avoid errors due to possible formation of amide the following experiments were carried out as rapidly as possible. In this experiment 0.2489 gram of metal was employed. Ammonia was withdrawn at 0° until the pressure nearly reached the dissociation pressure of the compound. There was found a gain of 0.6218 gram, corresponding to $n = 5.874$.

Experiment 3.—The calcium introduced weighed 0.2075 gram. After pumping off the excess solvent at 20°, there was found a gain of 0.5142 gram, giving $n = 5.825$.

Experiment 4.—In this experiment 0.5142 gram of metal was employed. The excess solvent was removed at 0° as in Experiment 2.

[1] *Loc. cit.*

There was found a gain of 1.2830 grams, from which n may be calculated to be 5.864.

After weighing, the tube was again attached to the pump and the ammonia was completely eliminated. The contents of the tube now weighed 0.0116 gram in excess of the weight of metal initially present. This indicates that amide is formed during the experiment. It was accordingly decided to carry out several experiments in which the solvent should be withdrawn at lower temperatures. It is to be mentioned, however, that at lower temperatures a longer time is required in removing the excess of solvent.

Experiment 5.—Employing 0.3888 gram of calcium from which the excess solvent was withdrawn at —33°, a gain of 0.9772 gram was obtained. This gives $n = 5.909$.

Experiment 6.—This experiment is a duplicate of No. 5. There was employed 0.4491 gram of metal and found a gain of 1.1255 grams. From these results n is found to be 5.891 molecules of ammonia per atom of calcium.

Collecting the results of the last five experiments we have:

Experiment No.	n.	Temperature.
2	5.874	0°
3	5.825	20°
4	5.864	0°
5	5.909	—33°
6	5.891	—33°

The temperatures here given are those at which the excess of ammonia was withdrawn. It is plain that at lower temperatures the value of n is consistently larger than at higher ones, while at the same temperature the results are in good accord. That a portion of the metal reacts with ammonia is indicated by the fact that a slow but steady increase in pressure may be observed, particularly at higher temperatures. We may conclude, therefore, that the composition of the compounds of calcium is represented by the formula $Ca(NH_3)_6$.

As already stated, Moissan describes a compound $Ca(NH_3)_4$. It might be though that the compound $Ca(NH_3)_6$ breaks down in two steps, in which case $Ca(NH_3)_4$ should appear as an intermediate product. The experiments described above show conclusively, however, that the compound dissociates according to the equation

$$Ca(NH_3)_6 \rightleftarrows Ca + 6NH_3 .$$

Compounds of Barium and Strontium.

A compound of barium, whose composition is $Ba(NH_3)_6$, has been described by Mentrel.[1] Systematic pressure determinations were not carried out for the purpose of determining the phase relations, but it is stated

[1] *Loc. cit.*

that above certain temperatures a solid compound is obtained which does not liquefy in excess of ammonia. It can scarcely be doubted, therefore, that a compound is formed. Employing the method of Joannis, he finds the decomposition decreasing from 6.97 molecules of ammonia per atom of metal at —50° to 6.10 at 0°. He believes the compound $Ba(NH_3)_6$ to be formed, the excess ammonia being present as a solid solution in this compound. There seems to be need of further evidence on this point.

Roederer[1] has investigated the action of ammonia on strontium. His results are in every way similar to those of Mentrel in the case of barium. He believes the compound $Sr(NH_3)_6$ to be formed. Here also the composition is a function of the temperature and a solid solution is suggested by way of explanation.

Nature of the Compound $Ca(NH_3)_6$.

It was stated at the beginning of this paper that Weyl, on discovering the solutions of sodium and potassium in ammonia, concluded that compounds resulted, to which he assigned an ammonium structure. Joannis, believing that he had isolated compounds of sodium and ammonia, retained these conceptions of Weyl as to the constitution, and other investigators have, for the most part, accepted this view. In the case of compounds containing a considerable number of ammonia molecules, the structural formulae advanced are rather complex to say the least, and they lack for support a single physical property or a single reaction that would indicate a structure such as has been proposed. How little this theory of constitution was based upon facts is well illustrated by the fact that those compounds which first led to the ammonium theory have now been shown to be non-existent. In the case of the metals of the alkaline earths where six molecules of ammonia are present per atom of metal and where all are given off at the same pressure, it is no longer necessary to take the ammonium theory into consideration. The term metal-ammonium should therefore be dropped from the literature as Ruff and Geisel have suggested.[1]

Before discussing further the question of the constitution of the compound $Ca(NH_3)_6$ it will be necessary to consider, briefly, the properties of this substance. It has already been mentioned that the compound is identical in appearance with the solution from which it is precipitated, *i. e.*, that it possessed the same optical properties. To whatever molecular condition these optical properties may be due, it is plain that they obtain in both solid and solution and are therefore not dependent on the physical state of the system. Now the compound and its solution not only possess the same optical properties but they likewise possess the same electrical properties, for both the solid and its solution exhibit

[1] *Loc. cit.*

metallic conduction. It seems possible, therefore, that the same factors which govern the optical properties of these two substances also govern their electrical properties. This suggests that if the factors governing the electrical and optical properties may be determined they will lead to some knowledge as to the state of the compound $Ca(NH_3)_6$ in its solid state. A further discussion of this point cannot be undertaken, however, until the data relating to the properties of the solutions in ammonia have been pesented.

That the compound $Ca(NH_3)_6$ is capable of existence is an important fact. We have here for the first time a compound in which a metal appears combined with a solvent without at the same time being combined with a strongly electronegative element or group of elements, as is commonly the case in solvated salts. The nature of the forces coming into play when calcium combines with ammonia must be quite different from those involved in the combination of a metal with a negative element to form a salt, for, while in the latter case all metallic properties are lost, in the former the metallic properties persist. The salts are usually considered to be valence compounds, and their formation is supposed to involve forces of an electric nature. The compound $Ca(NH_3)_6$ belongs to the class of compounds which, like the solvates, are commonly grouped under the head of molecular compounds. That electrical forces play only a minor part in the compound $(CaNH_3)_6$ is indicated by the persistence of the metallic properties.

It seems probable that the ammonia present in the calcium compound is combined with the metal in the same manner as in the case of ammoniated salts or solvated ions. Indeed the thought lies near that $Ca(NH_3)_6$ is simply a free positive ion which is present to some extent when a calcium salt is dissolved in ammonia. It is interesting, also, to note that this compound corresponds with both Abegg's theory of contravalences and Werner's co-ordination number.

Since the compound $Ca(NH_3)_6$ appears to be a solvate of the metal calcium, the name calcium, hexammoniate may be suggested as a consistent nomenclature.

Incidentally, attention may be called to the fact that the presence of a large number of nitrogen and hydrogen atoms in the compound does not interfere with its properties as a metal. The presence of non-metallic elements in a compound does not necessarily preclude the existence of metallic properties. Further examples of compounds of this character will be discussed later.

Summary.

The existing experimental data relating to the supposed formation of the compounds $NaNH_3$ and KNH_3 are examined in the light of the phase rule and the conclusion is reached that these compounds do not exist.

In a similar manner the non-existence of the compound $LiNH_3$ is established. In this case independent evidence is given which shows conclusively that in a system containing lithium and a small molecular per cent. of ammonia a saturated solution of the metal in ammonia is formed. This result is in agreement with the phase relationships existing in the system and demonstrates the inapplicability of the method employed by Moissan in obtaining and identifying the supposed compound of lithium and ammonia.

It is shown that calcium forms a solid compound with ammonia whose composition is represented by the formula $Ca(NH_3)_6$. The optical properties of this compound are apparently identical with those of its saturated solution in ammonia, and like its solution, the compound exhibits metallic conduction.

The vapor pressures of saturated solutions of lithium and of $Ca(NH_3)_6$ in ammonia have been determined, as well as the dissociation pressures of the compound itself. The heats of formation of the corresponding solutions and of the compound from metal and gaseous ammonia are calculated to be 8700, 10230, and 5460 calories per gram-molecule of ammonia, respectively.

The constitution of the compound $Ca(NH_3)_6$ is discussed. It appears that this compound is of the nature of a solvate, corresponding, perhaps, to an ammoniated calcium ion. It is suggested that the compound be called calcium hexammoniate in order to take account of these relations in the nomenclature.

BOSTON, February 6th, 1908.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. No. 25.]

THE OSMOTIC PRESSURE OF CONCENTRATED SOLUTIONS, AND THE LAWS OF THE PERFECT SOLUTION.

BY GILBERT NEWTON LEWIS.

Received March 5, 1908.

The laws of the infinitely dilute solution have been thoroughly established. There can be no reasonable doubt as to the accuracy of Henry's law for the vapor pressure of the solute, Raoult's law for the vapor pressure of the solvent, or van't Hoff's law for the osmotic pressure, in the case of an infinitely dilute solution. In fact if any one of these laws is shown to be correct, the other two must follow as a direct consequence of the laws of thermodynamics.

Unfortunately, we never work with an infinitely dilute solution, and too little attention has been given to the question of the validity or even the mutual compatibility of the laws just mentioned in concentrated solutions and even in the so-called dilute solutions.

There is a well known thermodynamic relation between the osmotic pressure of a solution and the lowering of the vapor pressure of the solvent, which enables us, in every case, regardless of the concentration of the solution, to calculate the osmotic pressure when the vapor pressure lowering is known, and *vice versa*. It is therefore possible to calculate the osmotic pressure of a given solution, first, on the assumption that van't Hoff's law[1] is correct, and second, on the assumption that Raoult's law[2] is correct. It is commonly supposed that for fairly dilute solutions these two methods of calculating the osmotic pressure give identical results, but this is not the case. For example, the osmotic pressures calculated in these two ways for a normal solution of cane sugar differ by 20 per cent. and even at the dilution of 0.005 normal the difference is still 0.1 per cent. It is obvious, therefore, that even in that region to which we are accustomed to apply the term, "dilute solution," the law of Raoult and the law of van't Hoff are not compatible. If one is true, the other must be false. What then shall we regard as an ideal or perfect solution, one that obeys the law of Raoult or one that obeys the law of van't Hoff, or shall we choose another criterion which differs from both of these?

Morse and Frazer,[3] who have recently succeeded in measuring osmotic pressures up to 25 atmospheres by a direct method, propose to replace the law of van't Hoff by the following equation, which gives values for the osmotic pressure more in accord with those obtained experimentally in the case of sugar and glucose:

$$\Pi = \frac{nRT}{V'}.$$

Here V' is not the volume of solution but the volume of pure solvent in which n mols of solute are dissolved. These authors propose, therefore, to substitute for the system in which concentrations are expressed in mols of solute in one liter of solution (volume normal system) another in which concentrations are expressed in mols of solute dissolved in one liter of pure solvent (weight normal system). In most cases the difference between these two systems is much less than it is in the case of the two substances of high molecular weight investigated by Morse and Frazer. Thus a weight normal solution of sugar is only 0.82 volume normal, a difference of about 20 per cent., but in the case of methyl alcohol, ammonia and hydrochloric acid, substances of small molecular weight se-

[1] $\Pi = nRT/V$, where Π is the osmotic pressure, R the gas constant, T the absolute temperature, and n is the number of mols of solute dissolved in the volume V of the solution.

[2] $(p_0 - p)/p_0 = n_1/(n+n_1)$, where p_0 is the vapor pressure of the solvent in the pure state, p that of the solvent from the solution, and n_1 is the number of mols of solute dissolved in n mols of solvent.

[3] *Amer. Chem. J.*, 34, 1 (1905); 37, 324, 425, 558; 38, 175 (1907).

lected at random for this calculation, the difference in concentration of weight normal and volume normal amounts to only 2, 4, and 2 per cent., respectively. It is fortunate, however, that they did study those very substances in which the difference between the two systems is most pronounced, for we are thus forced to face certain questions concerning moderately dilute solutions which have been too often evaded.

It will be the purpose of this paper not only to find what theoretical justification there may be for the above modification of the van't Hoff equation, but also to determine in general which of the various laws of solutions may be most suitably chosen to define the perfect solution.

Before beginning this inquiry it may be well to discuss briefly another question raised by Morse and Frazer, who write with some disparagement of the methods of determining osmotic pressure which rest upon thermodynamic calculations. Without undervaluing in any degree the importance of direct measurements of a quantity which has played so important a part in the development of modern chemistry as osmotic pressure, it must nevertheless be definitely affirmed that we have at our disposal several means of determining the osmotic pressure which are readily capable of furnishing results many times as accurate as any yet obtained by direct measurement. These methods will, therefore, be briefly considered in the following section:

Direct and Indirect Osmotic Pressure Measurements.

The exact definition of osmotic pressure, and some of the thermodynamic relations in which the osmotic pressure is involved will be discussed briefly in notes at the end of this paper. There it will be shown that the osmotic pressure of an aqueous solution may be obtained at once from the freezing point by means of the equation

$$\Pi = 12.06\Delta - 0.021\Delta^2, \qquad (1)$$

where Π is the osmotic pressure in atmospheres and Δ is the lowering of the freezing-point in centigrade degrees.[1] From this equation the osmotic pressure of any solution up to ten or fifteen times normal may be obtained with an accuracy which depends only upon the precision of the freezing-point determinations and upon the accuracy of the value used for the heat of fusion of ice. Since the error in the latter quantity

[1] If we assume that at infinite dilution van't Hoff's law holds exactly, and take R = 0.08207 liter atmospheres per degree, from the work of D. Berthelot (*Z. Elektrochem.*, 10, 621, 1904), then we find from equation (1) that the molecular lowering of the freezing-point of any aqueous solution at infinite dilution is 1.858°, which differs materially from the value commonly used, namely, 1.85. The latter value is used by Morse and Frazer, but they should use the value 1.843, for they do not employ the international atomic weights but those based on hydrogen as unity. The mol is therefore reckoned in the latter system, and not in the customary one, in Tables I and II where Morse and Frazer's data are used.

is probably not more than about 0.1 per cent., it is obvious that except for the most dilute solutions osmotic pressures may be found in this way with an accuracy which is more than ten times as great as Morse and Frazer claim for their direct measurements. It is interesting to compare the osmotic pressures obtained by Morse and Frazer with those calculated by equation (1) from the freezing-point measurement of the same authors. This comparison is made in Tables I and II. The first

TABLE I.—CANE SUGAR.

M.	Δ.	Π Obs.	Π Calc.	Per cent. difference.
0.1	0.195	2.44	2.35	4
0.2	0.392	4.80	4.73	1
0.3	0.585	7.16	7.05	2
0.4	0.784	9.40	9.45	1
0.5	0.985	11.8	11.8	0
0.6	1.19	14.2	14.3	1
0.7	1.39	16.8	16.7	0
0.8	1.62	19.3	19.5	1
0.9	1.83	22.1	22.0	0
1.0	2.07	24.8	24.9	0
0.867	1.77	.....	21.3	.
1.25	2.68	.....	32.2	.
1.54	3.42	.....	41.0	.
1.63	3.63	.....	43.5	.
2.10	4.88	.....	58.4	.

TABLE II.—GLUCOSE.

M.	Δ.	Π Obs.	Π Calc.	Per cent. difference.
0.1	0.192	2.40	2.32	3
0.2	0.386	4.65	4.65	0
0.3	0.576	7.01	6.94	1
0.4	0.762	9.30	9.18	1
0.5	0.952	11.6	11.5	1
0.6	1.15	14.0	13.8	1
0.7	1.34	16.4	16.1	2
0.8	1.53	18.8	18.4	2
0.9	1.72	21.2	20.7	2
1.0	1.92	23.6	23.1	2

column gives M, the number of mols of solute in one liter of water, the second the lowering of the freezing-point, the third the osmotic pressure directly measured, the fourth that calculated from Δ, and the fifth gives in round numbers the percentage difference between the observed and calculated values. In Table I, I have also given (below the line) the osmotic pressure of cane sugar solutions calculated from the freezing-point measurements of Ewan.[1] These seem in perfect accord with the values of Morse and Frazer and extend to higher concentrations. It

[1] *Z. physik. Chem.*, 31, 22 (1899).

is to be noted that each calculated value is obtained for the temperature at which the solution in question freezes, while the observed values were found at a few tenths of a degree above zero, but the correction for this small temperature difference is too small in comparison with the experimental errors to be considered.

It is apparent that the observed and calculated values for the osmotic pressure agree within the limits of error of the former. The tables indicate, moreover, that the experiments with glucose were somewhat less reliable than those with cane sugar.

Since, therefore, freezing-point measurements offer a simple and exact means of determining the osmotic pressure at the freezing-point, it is possible from them to determine the osmotic pressure at other temperatures, if we know its temperature coefficient. Morse and Frazer have considered it impossible to predict the value of this coefficient, but they have overlooked the simple thermodynamic equation, which may be derived immediately from the familiar energy equation of Helmholtz, namely,

$$\Pi - q = T\frac{d\Pi}{dT}, \tag{2}$$

where Π is the osmotic pressure, T the absolute temperature and q is the heat of dilution, that is, the heat evolved when one cc. of solvent is added to a large quantity of the solution. This quantity q is known for a large number of solutions and in any case may be very easily determined. For cane sugar we have very accurate knowledge of this quantity for one temperature, 15°, from the independent but entirely accordant work of von Stackelberg[1] and Ewan.[2] According to their measurements in the case of a weight normal solution q is equal to 0.12 cal. or 5 cc.-atmos. Substituting the latter value in equation (2) and calling Π at 15° approximately 24 atmos., which according to the experiments of Morse and Frazer cannot be far wrong, we find

$$\frac{d\Pi}{dT} = \frac{24-5}{273+15},$$

or about 0.07 atmos. per degree. In other words, while the osmotic pressure of an ideal solution at 15° changes 0.35 per cent. per degree the normal sugar solution changes only 0.27 per cent. per degree. Unfortunately we do not know the heat of dilution of sugar solutions at lower temperatures, but since in other cases von Stackelberg has shown that it increases with decreasing temperature, it is probable that it does in this case also. The temperature coefficient of osmotic pressure will therefore probably become smaller at lower temperatures and may even become negative (when $q > \Pi$), which would explain the surprising fact

[1] *Z. physik. Chem.*, 26, 533 (1898).

[2] *Loc. cit.*

discovered by Morse and Frazer that the osmotic pressure of cane sugar is about the same at 0° as it is at 25°.

Since the heat of dilution may be very readily measured at any temperature, we have by its means a remarkably simple method of determining the osmotic pressure at any temperature, if it is known at one.

For obtaining the osmotic pressure of a solution at any temperature there is another perfectly general indirect method which has been frequently employed[1] and recently has been improved to such a point that it rivals in accuracy the freezing-point method.[2] It depends upon the thermodynamic relation between the vapor pressure from a solution and the osmotic pressure, which may be expresssed in the equation[3]

$$\Pi - \frac{1}{2}\alpha\Pi^2 = \frac{RT}{V_0} ln \frac{p_0}{p}. \qquad (3)$$

Here Π is again the osmotic pressure, α is the coefficient of compressibility of the solvent, V_0 is its molecular volume, *ln* stands for natural logarithm and p_0 and p are respectively the vapor pressure of the solvent in the pure state and in the solution. Several applications of this equation will be made in the following section.

The Law of Ideal Solutions.

What we shall call a perfect or ideal solution is somewhat a matter of choice. We might define as an ideal solution one which obeys the law of van't Hoff, or the modified form of this law proposed by Morse and Frazer, or the law of Raoult, or the law of Henry. These laws are essentially identical for the infinitely dilute solution, but for a solution of finite concentration we are at liberty to choose one but not all of these laws to define the ideal solution. No one of them is true for every solution at every concentration, and we must therefore choose that one which holds most nearly for the greatest number of substances over the widest limits of concentration.

I shall attempt to show that the most fundamental law of solutions and the one by which the perfect solution is best defined is the following modification of the law of Raoult. *At constant pressure and temperature the activity*[4] *of the solvent in a perfect solution is proportional to its mol fraction.* That is,

$$\xi = \xi_0 N, \qquad (4)$$

where ξ is the activity of the solvent in the solution, ξ_0 the activity of the pure solvent, and N, the mol fraction, is the number of mols of sol-

[1] See for example, Noyes and Abbott, *Z. physik. Chem.*, **23**, 56 (1897).

[2] See Smits, *Z. physik. Chem.*, **51**, 33 (1905).

[3] For the development of this equation, see note 3, at the end of this paper.

[4] For a definition of the term activity see Lewis, "Outlines of a New System of Thermodynamic Chemistry," *Proc. Amer. Acad.*, **43**, 259 (1907); and *Z. physik. Chem.*, **61**, 129 (1907); *C. A.*, **1908**, 611.

vent in one mol altogether of solvent and solute. Since, however, the conception of activity is new, and since if the vapor of the solvent obeys the gas law the activity is proportional to the vapor pressure, we may with sufficient exactness for our present purposes, substitute the vapor pressure of the solvent for its activity and write

$$p = p_0 N; \tag{5}$$

that is, in a perfect solution the vapor pressure of the solvent is proportional to its mol fraction.[1] Thus in a solution containing 0.1 mol solute to 0.9 mol solvent, $N = 0.9$ and the vapor pressure of the solvent should be nine-tenths of its vapor pressure in the pure state, or if the solution contains 0.25 mol solute to 0.75 mol solvent p should be $0.75\ p_0$. This is simply a statement of Raoult's law in its simplest form.[2]

There are no cases in which the law of van't Hoff or the modified form of this law proposed by Morse and Frazer have been shown to hold at concentrations higher than normal. (In a normal solution in water the mol fraction of the solute is about 0.02.)

Indeed, at very high concentrations van't Hoff's law cannot hold, for the osmotic pressure of a solution approaches infinity as the percentage of solvent approaches zero, while the osmotic pressure calculated from the van't Hoff equation never exceeds a few hundred atmospheres even when we approach the condition of pure solute. On the other hand, it will be shown presently that the law proposed by Morse and Frazer ordinarily gives, at higher concentrations, osmotic pressures far higher than those which actually exist. But often the law of Raoult (and the modified law of Henry) has been shown to hold *at all concentrations from 0 per cent. to 100 per cent. of solute*, and while in many other cases this

[1] The point of view here adopted is practically identical with that which for several years has been advocated by J. J. van Laar in numerous publications.

[2] It is important to note that equation (4) leads us immediately to a simple equation for the activity or the vapor pressure of the solute. In the paper previously referred to I have proved the following exact equation for the change in the activity of each component of a binary mixture with change of composition, namely,

$$N_1 d\ln\xi_1 + N d\ln\xi = 0,$$

where N_1 is the mol fraction and ξ_1 the activity of one constituent which we will call the solute, and N and ξ are the corresponding terms for the other constituent which we will call the solvent. Now, when equation (4) is true, $d\ln\xi = d\ln N$. Substituting in the above equation and noting that by definition $N_1 = 1 - N$ we find

$$N_1 d\ln\xi_1 + dN = 0, \text{ or,}$$

$$d\ln\xi_1 = d\ln N_1, \text{ or}$$

$$\xi_1 = KN_1,$$

where K is a constant. We see therefore that in a perfect solution it is also true that the activity of the *solute* is proportional to its mol fraction. If we substitute p_1, the vapor pressure of the solute, for ξ_1, $p_1 = KN_1$, which is, in a slightly modified form, the law of Henry. In other words, if both vapors obey the gas law, the law of Henry may be derived thermodynamically from the law of Raoult and must hold if that law does.

law does not hold, the greatest deviations are always found in those cases in which we have reason to believe that the solvent and the solute form complex compounds either with themselves or with each other.

Many illustrations might be given to show the remarkable scope of Raoult's law. I will choose a binary mixture which has been studied more carefully over a wide range of concentration than any other, namely, benzene and ethylene chloride. The vapor pressures are taken from the excellent paper of Zawidski.[1] We will call benzene the solvent and ethylene chloride the solute. In Table III, in which the data marked by Zawidski as questionable are omitted, the first column gives the number of grams of solute to one gram of solvent, the second gives the partial vapor pressure of the solvent at 50°, and the third gives the molecular weight of ethylene chloride calculated from the vapor pressures by Raoult's law. The calculated molecular weights are constant, even up to the highest concentration, where the solute constitutes over 90 per cent. of the solution. The average of these calculated molecular weights is 99.1 while the actual molecular weight of ethylene chloride is 99.0. (We have therefore every ground for believing that also in the pure state ethylene chloride exists in the form of simple molecules.)

TABLE III.

Grams $C_2H_4Cl_2$ to 1 g. C_6H_6.	p. of C_6H_6.	M. W. $C_2H_4Cl_2$.
0.0	268.0	....
0.525	189.8	99.4
0.904	156.0	98.2
1.39	127.8	98.7
2.43	92.4	99.3
3.89	65.9	99.0
14.54	21.8	100.0
	Average,	99.1
	Theoretical,	99.0

If then we define a perfect solution as one which obeys Raoult's law,[2] it is interesting to find what the law is connecting osmotic pressure and concentration in a perfect solution. This law, which is less simple than either the law of van't Hoff or that of Morse and Frazer, may be derived directly from equations (3) and (5), and is

$$\Pi - \frac{1}{2}\alpha\Pi^2 = -\frac{RT}{V_0} ln N \qquad (6)$$

or

[1] *Z. physik. Chem.*, 35, 129 (1900).

[2] Strictly speaking, we define a perfect solution as one which obeys equation (4) rather than equation (5), but the more precise method which employs the activity instead of the vapor pressure leads to exactly the same equation for the osmostic pressure as we shall derive here.

$$\Pi - \frac{1}{2}\alpha\Pi^2 = -\frac{RT}{V_o} ln(1 - N), \qquad (7)$$

where V_o is the molecular volume and α the compressibility of the solvent.

In Table IV the osmotic pressures of cane sugar solutions are calculated from equation (7). The first column gives the weight normal concentration; the second, the volume normal; the third, N_1, the mol fraction of solute; the fourth, the osmotic pressures calculated by the van't Hoff equation; the fifth, those calculated by the equation of Morse and Frazer; the sixth, those calculated by equation (7); the seventh, Morse and Frazer's observed values.

TABLE IV.

Conc. wt. norm.	Conc. vol. norm.	Mol fraction of solute.	Π van't Hoff.	Π Morse and Frazer.	Π Lewis.	Π Observed.
0.1	0.098	0.00180	2.34	2.41	2.41	2.40
0.2	0.192	0.00358	4.58	4.81	4.80	4.74
0.3	0.282	0.00537	6.73	7.23	7.21	7.23
0.4	0.369	0.00715	8.81	9.64	9.60	9.67
0.5	0.452	0.00892	10.8	12.0	12.0	12.1
0.6	0.532	0.0107	12.7	14.5	14.4	14.4
0.7	0.610	0.0124	14.5	16.8	16.7	16.9
0.8	0.684	0.0142	16.3	19.3	19.2	19.4
0.9	0.756	0.0159	18.1	21.7	21.5	21.8
1.0	0.825	0.0177	19.7	24.1	23.9	24.5

While the values given by the equation of van't Hoff differ from those observed by nearly 25 per cent. at the higher concentrations, it will be seen that the pressures given in the fifth and sixth columns agree throughout with the observed values, within the limits of experimental error, and differ from each other by only one per cent. even at normal concentration.

This agreement between the osmotic pressures calculated from the equation of Morse and Frazer and those calculated by equation (7) will always be found at moderate concentrations, as the following considerations show. The second term in equation (7), except at the very highest concentrations, is comparatively insignificant, amounting usually to only a few per cent. of the value of Π even when the osmotic pressure is as high as a thousand atmospheres. At moderate concentrations we may, therefore, neglect this term and write equation (7) in the form,

$$\Pi = -\frac{RT}{V_o} ln(1 - N_1). \qquad (8)$$

Now the equation of Morse and Frazer may be written in the form

$$\Pi = \frac{RT}{V_o}\left(\frac{N_1}{1 - N_1}\right), \qquad (9)$$

for $\frac{N_1}{1-N_1}$ is the number of mols of solute to one mol of solvent and V_0 is the volume of one mol of pure solvent.

Equation (8) developed in series gives

$$\Pi = \frac{RT}{V_0}\left(N_1 + \frac{1}{2}N_1^2 + \frac{1}{3}N_1^3 + \ldots\right),$$

and similarly equation (9) gives,

$$\Pi = \frac{RT}{V_0}\left(N_1 + N_1^2 + N_1^3 + \ldots\right).$$

These equations differ only in the higher powers of N_1 and therefore give identical results at such concentrations that the terms containing these higher powers are negligible. When the mol fraction of the solute is 0.02 the values of Π calculated from these equations differ by one per cent. For all more dilute solutions, therefore, the osmotic pressure of a perfect solution may be calculated within one per cent. from the equation of Morse and Frazer.

At higher concentrations, however, the difference between these two equations becomes very great, as is shown in Tables V and VI. Table V deals with solutions of ethylene chloride in benzene, and simply restates in a new way the facts brought out in Table III. Table VI contains data on solutions of propylene bromide in ethylene bromide. In both tables the first column gives the mol fraction of solute; the second, the partial yapor pressure of the solvent, taken from the work of Zawidski;[1] the third, the osmotic pressure calculated by the van't Hoff equation; the fourth, that calculated by the equation of Morse and Frazer; the fifth, that calculated by equation (7), while the last column gives the actual osmotic pressure obtained thermodynamically from the vapor pressures by means of equation (3). The molecular volumes of benzene and ethylene chloride at 50° are taken, respectively, as 0.092 and 0.082 liter, and the coefficient of compressibility of benzene as 0.0001. The molecular volumes of ethylene and propylene bromides at 85° are taken, respectively, as 0.092 and 0.113 liter, and the coefficient of compressibility of ethylene bromide as 0.000,06.

TABLE V.

$C_2H_4Cl_2$ in C_6H_6 at 50°.

N_1.	p_2.	Π. van't Hoff.	Π. Morse and Frazer.	Π. Lewis.	Π. Found.
0.0	268.0	..	..	..	..
0.293	189.8	91	120	101	100
0.416	156.0	128	205	157	158
0.522	127.8	160	315	215	217
0.657	92.4	196	549	313	310
0.754	65.9	223	880	413	406
0.920	21.8	268	3290	743	735

[1] Omitting the values which the author marks as questionable.

TABLE VI.

$C_2H_6Br_2$ in $C_2H_4Br_2$ at 85°.

N_1.	p_2.	II. van't Hoff.	II. Morse and Frazer.	II. Lewis.	II. Found.
0.0	172.6	..	..	..	..
0.147	145.1	47	55	51	55
0.222	132.2	69	91	80	86
0.298	121.1	90	136	113	114
0.412	101.1	121	224	171	173
0.526	81.9	150	351	241	240
0.620	64.0	173	520	313	319
0.720	48.0	198	820	412	414
0.800	34.3	218	1280	522	525
0.860	23.5	232	1960	640	649
0.915	13.8	241	3440	806	827

We see from these tables how closely in these two cases the actual osmotic pressures agree with those calculated by equation (7), and how far from the truth are the pressures calculated both by the van't Hoff equation and by that of Morse and Frazer. These two solutions are, according to our definition, perfect solutions, within the limits of experimental error, for all concentrations from 0 to over 90 per cent. of solute. Since, moreover, these cases are not unique but have been chosen out of a large number of similar cases merely because of the greater experimental care with which they have been investigated, it is to be presumed that even those solutions which are not perfect at all concentration will, on the average, follow the law expressed in equation (7) to higher concentrations than they will the law of van't Hoff or that of Morse and Frazer.

In view of the experiments of Morse and Frazer, it has recently been proposed[1] that in the ordinary equations of chemical equilibrium the concentrations expressed in the volume normal system should be replaced by those expressed in the weight normal system. This is undoubtedly an improvement, but the equations thus obtained are not entirely correct, even when all the substances concerned are present as perfect solutions.

In order to find an exact equation, let us consider a reaction occurring as follows:

$$x_1X_1 + x_2X_2 + \ldots = x_3X_3 + x_4X_4 + \ldots,$$

where x_1 mols of X_1 combine with x_2 mols of X_2 to form x_3 mols of X_3, etc. It is readily seen from the considerations advanced in this paper and from the thermodynamic laws of chemical equilibrium,[2] that the general equation of chemical equilibrium, regardless of the concentra-

[1] Walden: *Z. physik. Chem.*, 58, 500. This paper also contains a letter from van't Hoff on this subject.

[2] Lewis: *Loc. cit.*, equation (XXIII).

tions of the reacting substances, provided that they are all present as perfect solutions, is as follows:

$$\frac{N_3^{x_3}N_4^{x_4}\ldots}{N_1^{x_1}N_2^{x_2}\ldots} = K \text{ (a constant)}, \qquad (10)$$

where N_1, N_2, etc., are the respective mol fractions of X_1, X_2, etc.

This, then, is the form which the mass law assumes when the substances concerned form perfect but not infinitely dilute solutions, and for such cases it is rigorously exact.

Note 1.

If a solution and the pure solvent are separated by a semipermeable membrane the solvent will flow through the membrane into the solution, where its escaping tendency is less. The only way of preventing this flow is to make the escaping tendency of the solvent the same on both sides of the membrane. There are two simple ways of accomplishing this, (1) to increase the pressure on the solution until the escaping tendency of the solvent in the solution is raised to equal that of the solvent in the pure state, (2) to diminish the pressure on the pure solvent until its escaping tendency is lowered to equal that of the solvent in the solution.

The osmotic pressure may therefore be defined in two ways, (1) as usually defined it is the increase in the pressure on the solution necessary to bring the latter into equilibrium with the solvent; (2) Noyes,[1] however, prefers to define the osmotic pressure as the diminution in the pressure on the solvent necessary to bring it into equilibrium with the solution. Neither of these definitions is entirely free from objections, but since the second one permits a much simpler mathematical treatment than the first, it has been adopted throughout this paper. The osmotic pressures defined in these two ways differ only when there is a total change of volume when a small quantity of solvent is added to a solution. There is no such volume change in the case of sugar and glucose as shown by the experiments of Morse and Frazer and of Ewan. We have been justified, therefore, in applying our equations, which involve the osmotic pressure according to the second definition, to the results of Morse and Frazer, who worked with the osmotic pressure of the first definition.

Note 2.

The exact equation connecting osmotic pressure and freezing-point may be found as follows: Let us consider an aqueous solution in equilibrium with ice at the temperature T and the pressure p, and also in equilibrium with these, through a semipermeable membrane, pure water at the same temperature and at the pressure $p - \Pi$, Π obviously being the osmotic pressure. Now if the temperature changes by dT and the pres-

[1] *Z. physik. Chem.*, 35, 707 (1900).

sure on the solution and ice remains equal to P, that on the water must be changed in order to maintain equilibrium. The necessary change in pressure we will call $d\Pi$. Since the water and ice are in equilibrium at the beginning, the activity ξ of the water and the activity ξ' of the ice must be equal, and these, moreover, must remain constant as the temperature changes. Hence,

$$\xi = \xi'$$

and

$$d\xi = d\xi'$$

or,

$$dln\xi = dln\xi'.$$

Now the change in the activity of the ice is due only to the change of temperature, that is,

$$dln\xi' = \left(\frac{\partial ln\xi'}{\partial T}\right)dT,$$

but the activity of the water is changed both by the change in temperature and the change in pressure, that is,

$$dln\xi = \left(\frac{\partial ln\xi}{\partial T}\right)dT + \left(\frac{\partial ln\xi}{\partial \Pi}\right)d\Pi.$$

Equating the last members of these two equations, we have

$$\left(\frac{\partial ln\xi'}{\partial T}\right)dT - \left(\frac{\partial ln\xi}{\partial T}\right)dT = \left(\frac{\partial ln\xi}{\partial \Pi}\right)d\Pi.$$

Now substituting for the partial differentials their values from the fundamental thermodynamic equations[1] and combining the first two terms gives

$$\frac{d\Pi}{dT} = \frac{-L}{vT},$$

where L is the heat absorbed in the fusion of one gram of ice and v is the volume of one gram of water. For T we may substitute $273.1 - \Delta$, where Δ is the lowering of the freezing-point below the centigrade zero, whence

$$\frac{d\Pi}{d\Delta} = \frac{L}{v(273.1 - \Delta)}.$$

In order to integrate this equation, L and v must be known as functions of Δ. According to a well-known principle the change of L with Δ is given by the equation

$$L = L_0 - C\Delta,$$

where L_0 is the heat of fusion at 0° C. and C is the difference between the specific heats of water and ice. According to the best available data, C is about 0.5 if our unit of energy is the calorie, or 21 if our unit of energy is the cc.-atmos. The value of L_0 obtained in the very ac-

[1] Lewis: *Loc. cit.*, equations V and VIII. It is of course to be noted that by definition Π is a negative pressure.

curate experiments of Smith[1] was 334.2 joules, assuming the electromotive force of the Clark cell to be 1.434 V at 15°. Since this value entered twice into the calculation of Smith, if we adopt for the Clark cell the value now accepted of 1.433 V, the value of L_0 must be lowered by 2 parts in 1434 and becomes 333.7 joules, or 3294 cc.-atmos.[2]

We may therefore write,

$$L = 3294 - 21\Delta.$$

Strictly speaking, L is a function of the pressure also, but the pressure effect may easily be shown to be too small to be considered in the present calculation.

The volume of a gram of water also depends upon both temperature and pressure. We shall see that one degree lowering of the freezing-point corresponds to about 12 atmos. change in the osmotic pressure. Hence from the known coefficients of thermal expansion and compressibility we find that the value of v may be expressed very closely by the linear equation,

$$v = 1.000 + 0.0008\Delta.$$

Substituting now in the above equation the values of L and v, and performing the multiplications and divisions indicated, we obtain $\frac{d\Pi}{d\Delta}$ as a series function of Δ, namely,

$$\frac{d\Pi}{d\Delta} = 12.06 - 0.0414\Delta - 0.00009\Delta^2 + \ldots.$$

Except for very high values of Δ and Δ^2 term and all the higher terms are negligible. Dropping these terms, therefore, and integrating, we have

$$\Pi = 12.06\Delta - 0.21\Delta^2.$$

By this equation the osmotic pressure corresponding to any freezing-point lowering may be calculated immediately and, if the experimental data used are as accurate as they appear, the error of the calculation can hardly exceed a few tenths of a per cent. even at osmotic pressures of several hundred atmospheres.

Note 3.

The connection between the osmotic pressure and the vapor pressure of the solvent from a given solution is obtained as follows: From the fundamental thermodynamic equation for the change of the activity of a substance with the pressure,[3] we have

$$\frac{dln}{d\Pi} = \frac{-V}{RT},$$

[1] *Phys. Rev.*, 17, 231 (1903).

[2] Guttmann (*J. Phys. Chem.*, 11, 279 (1907)) has made a similar recalculation of Smith's value but applied only one-half of the correction applied above.

[3] Lewis: *Loc. cit.*, equation V.

where V is the molecular volume and ξ is the activity of the pure solvent. When the vapor of the solvent behaves like a perfect gas whose pressure is p we may write

$$dln\xi = dlnp.$$

Hence, in such a case,

$$\frac{dlnp}{d\Pi} = \frac{-V}{RT}.$$

V may be regarded as constant for small values of Π but at high pressures we must consider the compressibility of the solvent. If the coefficient of compressibility of the solvent is denoted by α, and the volume when the osmotic pressure is zero by V_o,

$$V = V_o(1 - \alpha\Pi).$$

Substituting this value of V in the above equation and integrating, we have

$$\Pi - \frac{1}{2}\alpha\Pi^2 = \frac{RT}{V_o} ln\frac{p_o}{p},$$

where p_o is the vapor pressure of the pure solvent, p that of the solvent in the solution of osmotic pressure Π. This equation is derived for the case that the vapor of the solvent obeys Boyle's law. In any other case a more complicated formula must be used.

Summary.

The simple laws of the infinitely dilute solution become mutually incompatible in solutions of finite concentration. It is therefore necessary to choose one law to serve as a criterion of the perfect solution. The only law of dilute solutions which ever holds in concentrated solutions is the law of Raoult. This law is stated in a slightly modified form and a perfect solution is defined as one which obeys this law. A number of solutions are mentioned which behave as perfect solutions over the whole range of concentrations, from 0 per cent. to 100 per cent. solute.

The indirect methods of determining osmotic pressure are discussed and an exact relation between the osmotic pressure and the freezing-point lowering of an aqueous solution is obtained. It is also pointed out that the osmotic pressure at one temperature may be obtained from that at any other when the heat of dilution is known.

Adopting Raoult's law in its modified form as the characteristic law of the perfect solution, it is possible with the aid of thermodynamics alone to obtain an equation connecting the osmotic pressure and concentration of a perfect solution. The equation thus obtained permits the exact calculation of osmotic pressures in perfect solutions, up to 1000 atmos. In comparatively dilute solutions the pressures thus obtained are substantially identical with those given by the equation of van't

Hoff, as modified by Morse and Frazer, but at high concentrations the divergence between the two equations is very great.

An exact form is obtained for the mass law in concentrated perfect solutions.

BOSTON, March 2, 1908.

[CONTRIBUTION FROM ROGERS'S LABORATORY OF PHYSICS OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE INDESTRUCTIBILITY OF MATTER AND THE ABSENCE OF EXACT RELATIONS AMONG THE ATOMIC WEIGHTS.

BY DANIEL F. COMSTOCK.

Received March 9, 1908.

The two chief reasons briefly stated for believing in the evolution of the elements one from another are, first, that some such process is undoubtedly taking place in the case of the radioactive substances, while we are being forced toward the conclusion that all the elements are radioactive to some degree; and second, that in the hottest stars only two known elements occur, namely, hydrogen and helium, while as we pass successively to cooler and cooler stars the other elements gradually make their appearance in a more or less orderly manner. Apparently this can only mean that at these transcendental temperatures the forces due to molecular or atomic impact are comparable with the interatomic forces involved in the breaking up of one element to form another, and hence the combination necessary for the formation of the heavier elements can take place only after the temperature has sufficiently dropped.

There is one seemingly fatal objection, however, to any very simple statement of the evolutionary theory and this objection has not been sufficiently emphasized. The difficulty is this, that so far as we know there are no exact simple relations between the various atomic weights, whereas if we are to assume, as the simplest form of the evolutionary theory does, that the lighter elements come from an atomic disintegration of the heavier ones, or *vice versa*, it is evident that simple additive relations must exist.

As we know, many simple, additive relations do exist, but they are approximate, not exact, and the deviations from exactness, though small, are larger than we can explain from error in atomic weight determinations.

On the basis of common conceptions, therefore, the evidence seems contradictory, certain facts seeming to require the simple evolutionary idea, while another fact, the inexactness referred to above seeming to deny it.

I wish to show that on the basis of the electrical constitution of matter this inexactness is not only to be explained but it is to be expected.

By the electrical constitution of matter is meant merely that conception, which has grown in favor among physicists of late, which considers the atom to consist wholly or in part of a group of electric charges. Some of these make themselves evident in an ionized electrolyte or in a gas, but in general the fact that the two electricities, positive and negative, are present in equal amounts makes the atom neutral as regards action on an outside point.

Now since moving charges always act like currents, and hence must set up magnetic fields, it must follow that when an apparently uncharged atom is set in motion there will be set up inside of it a magnetic field, which depends for its strength and distribution on the number, position, and magnitude of whatever charges the atom may be supposed to contain. It will therefore require more energy to set the atom in motion because of the necessity of building up this field, and hence the atom will have an added inertia, *i. e.*, an added mass because of these charges.

Now it has been shown mathematically by the author (*Phil. Mag.*, Jan., 1908), without making any assumption as regards the structure of the atom, that *this added mass due to the electric charges is strictly proportional to the total electrical energy contained in the atom.*

By electrical energy is meant the energy which we know must exist in space wherever there are electric lines of force. Two charges, one positive and one negative, attract each other, and if these are separated to a distance, work must be done against their mutual attraction. Since the charges themselves have changed in no way, the energy put in must exist in the surrounding space in a form generally known as "strain in the ether." Magnetic lines of force also correspond to energy stored in space and the statement proved in the paper mentioned above is that the added mass which an atom possesses because of the electric charges which it is supposed to contain depends only on the total electric and magnetic energy which the atom contains and is directly proportional to this energy.

The expression found may be written

$$M = \frac{4}{3}\frac{E}{V^2}$$

where M is this "electric mass," V is the velocity of light, and E is the total contained electromagnetic energy of the kind described above.

The amount of energy which corresponds to a gram mass is enormous. It is readily calculated from the formula, and is found to be 7×10^{20} ergs, approximately, so we may make the statement that, on the present bases, *the inertia of a gram mass is due to the existence within it of* 7×10^{20} *ergs of confined energy.*

Now, when the atom of an element breaks up the process is a violent one and a large quantity of energy is lost, *i. e.*, goes ultimately into heat.

Hence, if this is electric energy lost—and on the basis of the electrical conception it *is* electrical energy—it follows from the above that *there must have been a loss in mass accompanying the atomic disintegration* because of the energy lost. Hence, taking the simple case of an atom of A, splitting up violently and forming atoms of the elements B and C, we would find that the mass of B and C, taken together, would be a little less than the mass of A, from which they came, the difference corresponding to the loss of mass accompanying the loss in energy.

Now the loss of energy when an atom of radium breaks up is known, and calculation shows that this would give a loss in mass which would be of about the same size as the deviations in atomic mass or weight so common in the table.

In an important paper[1] Rydberg has shown that the atomic weights of the first twenty-seven elements of the periodic system approximate to whole numbers very much more closely than chance could bring about. He has also shown that the atomic weights of these elements are best considered as the sum of two parts (N + D), where N is an integer and D is a fraction, in general positive and smaller than unity. If M is the number of the element in the system (called by Rydberg the "Ordnungszahl"), then N is equal to 2M for the elements of even valence and 2M + 1 for the elements of odd valence. Below is given a table showing the various quantities. I have used, however, the International Atomic Weight values for 1907 instead of those Rydberg used.

Sign.	M.	N. 2M.	N. 2M + 1.	Atomic weight.	D.	Sign.	M.	N. 2M.	N. 2M + 1.	Atomic weight.	D.
He.....	2	4		4		P.....	15		31	31.0	0
Li.....	3		7	7.03	0.03	S.....	16	32		32.06	0.06
Be.....	4	8		9.1	1.1	Cl.....	17		35	35.45	0.45
B.....	5		11	11.0	0	A.....	18	36		39.9	3.9
C.....	6	12		12.00	0	K.....	19		39	39.15	0.15
N.....	7		15	14.01	—0.99	Ca.....	20	40		40.1	0.1
O.....	8	16		16.00	0	Se.....	21		43	44.1	1.1
Fl.....	9		19	19.0	0	—	22	44		...	...
Ne.....	10	20		20.0	0	—	23		47	...	...
Na.....	11		23	23.05	0.05	Ti.....	24	48		48.1	0.1
Mg.....	12	24		24.36	0.36	V.....	25		51	51.2	0.2
Al.....	13		27	27.1	0.1	Cr.....	26	52		52.1	0.1
Si.....	14	28		28.4	0.4	Mn.....	27		55	55.0	0.0
						Fe.....	28	56		55.9	—0.1

Many besides Rydberg have, of course, noticed and studied the curious deviations in the table of atomic weights and Rydberg's work is mentioned merely because it seems unusually explicit.

The orderly arrangement of the series is striking. It will be noticed

[1] *Z. anorg. Chem.*, 14, 66 (1897).

that in three cases only are the D's greater than unity and only in two cases are they negative.

Rydberg points out that although the heavier elements do not conform well to this scheme, *i. e.*, do not in general give the small fractional, values of (D) noticed above, yet this is in reality no valid objection, for the numerical values of the weights of heavier elements depend much more on the value of the arbitrary unit chosen than do those of the lighter weight elements, and hence they can have little influence one way or the other in estimating the validity of the curious relations he sets forth.

The whole question is, of course, whether these differences represent real physical deviations from something or whether they are merely mathematical remainders. Rydberg certainly believes them to represent physical realities, and considering the before-mentioned overwhelming improbability that the approximation of the atomic weights to whole numbers is due to chance, we can hardly doubt that he is right.

The question will doubtless be asked why is there no loss of mass found when a violent chemical reaction takes place and energy is lost. The expression for loss of mass in terms of loss of energy, when written in the differential form (substituting $V = 3.10^{10}$) is

$$\Delta M = \frac{4}{27} 10^{-20} \Delta E,$$

and if we substitute the heat of reaction of any known chemical reaction for ΔE, we find that ΔM is too small to be detected even by the delicate experiments of Landolt.

For the reaction

$$O_2 + 2H_2 = 2H_2O,$$

ΔM for one gram molecule is about 10^{-10} of a gram.

In radioactive changes, however, the energy is enormously greater and hence is to be detected as before mentioned.

If we consider the whole atom is electric instead of only part, as we have considered above, a conception which is by no means artificial since it has been proven that the mass of an electron is entirely due to its charge, we reach the interesting conclusion that on this basis the "Indestructibility of Matter" is only a corollary of the "Conservation of Energy," for if the atoms are to be considered as electrical systems it follows that the law of the Conservation of Mass, which is essentially the same as the Indestructibility of Matter, must be approximately true, though not strictly true. It must be approximately true because no known chemical or physical change, with the exception of radioactivity, involves anything but a relatively minute liberation or absorption of energy, but the law cannot be absolutely exact, for even this minute loss of energy must involve, on the present basis, its corresponding loss of mass. Thus even

the cooling of a hot body must involve a certain diminution of mass, though this, of course, is extraordinarily small, much smaller even than the loss due to most chemical reactions.

It would be interesting to search for other evidence of the existence of this vast store of energy in matter. Such evidence would involve effects, which would be approximately proportional to the density. Such an effect is found in the case of the absorption of the β-rays of radium when passing through different kinds of matter. Here the absorption is proportional to the density over a very wide range. Strutt has shown that in the case of fourteen substances whose absorption he measured, where the density varied from 0.007 in the case of sulphur dioxide, to 21.5 in the case of platinum, the ratio of the absorption to the density has an average deviation of only 20 per cent.

From a physical point of view, also, it is interesting to note that, since gravitation has always been found to be strictly proportional to mass, it follows from the above that the electrical structure of matter requires that gravitation should be proportional to the energy contained in the gravitating bodies and to this energy alone. Thus gravitation must be considered on the present basis as existing between quantities of confined, electromagnetic energy and not between "masses" in any other sense. More knowledge bearing on the electrical theory of matter would therefore throw considerable light on the outstanding mystery of gravitation.

Summary.

We have seen that, assuming the electrical theory of matter—the theory, that is, which considers the atoms as systems composed of electric charges—it follows that the mass of a piece of matter is determined solely by the amount of electromagnetic energy which it contains and is proportional to this amount. The energy in ergs which endows one gram with its mass is equal to three-fourths of the square of the velocity of light, or, in round numbers, twenty million horse-power-hours, or the energy corresponding to the work of one thousand horses working for two years. This enormous amount is by no means impossible since the amount of energy which the radioactive substances are known to *lose* in passing to lower forms is quite appreciable in comparison.

On the electrical theory of matter it therefore follows that the chief property of matter, the property which gives us a quantitative definition, namely its inertia or mass, is really a property of the energy stored up within the structure which defines the space relations of a piece of matter and is not a property of the structure itself. Thus it follows that the law of the "Conservation of Mass," which we have here reason to believe is only approximate, is in reality a corollary to the law of the

"Conservation of Energy" and thus this latter law and the "Indestructibility of Matter" are closely akin.

From the above it follows that on the present basis any loss of energy must involve a decrease in mass. Thus when a chemical reaction which liberates heat has taken place, when a body is cooled or when by the process of radioactivity one substance loses energy and is transformed into another substance, there must be a decrease in the mass of the whole and hence also a decrease in weight. In the first two cases mentioned, however, the change is too small to be detected but in the last case the change should be appreciable, and we have a ready explanation of the irregularities which occur in the table of atomic weights.

Finally, it is pointed out that since gravity is proportional to mass it would appear that gravitation must be considered as acting between quantities of confined energy and not between "masses" in any other sense.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]

TWO NEW METHODS FOR THE DETERMINATION OF THE SECONDARY IONIZATION CONSTANTS OF DIBASIC ACIDS.

BY HERBERT N. MCCOY.

Received March 3, 1908.

The ionization of a dibasic acid, H_2X, takes place in two stages, represented by the following equations:

$$H \cdot HX = k_1 H_2X; \quad (1)$$

$$H \cdot X = k_2 HX; \quad (2)$$

where k_1 and k_2 are the ionizaton constants, and where the formulae represent the molar or ionic concentrations of the corresponding substances. With the exception of a few moderately strong acids, like oxalic, all organic dibasic acids are found by conductivity measurements to dissociate essentially according to equation (1), in solutions more concentrated than milli-normal; they thus behave like monobasic acids.[1] The second constant, k_2, is always much smaller than the first. While the secondary ionization produces but a negligible effect in solutions of the free acid, in solutions of the acid salts its effect is of great importance.

When an acid salt, like NaHX, is dissolved in water it reacts, partially, forming the free acid and the neutral salt, according to the equation, thus:

$$2NaHX \rightleftarrows H_2X + Na_2X.$$

The state of equilibrium reached is governed by equations (1) and (2), which, by combination, give

[1] Ostwald: *Z. physik. Chem.*, 3, 281 (1889).

$$\frac{HX^2}{H_2X \cdot X} = \frac{k_1}{k_2}. \qquad (3)$$

Equation (3) applies to solutions containing all proportions of acid, acid salt and neutral salt, as well as to solutions resulting from the pure acid salt and water. I have found[1] that the equilibrium in solutions of the carbonates of sodium is accurately represented by the relationship

$$\frac{NaHCO_3^2}{H_2CO_3 \times Na_2CO_3} = \text{a constant.} \qquad (3a)$$

Where the formulae now represent the total concentrations of the respective substances, Equation (3*a*) becomes identical with (3) for very dilute solutions, in which the salts are practically completely ionized. For a fixed concentration of total sodium, a good constant was found for all proportions of carbonate, bicarbonate and carbonic acid. The concentration of the later component was proportional to the concentration of the gaseous carbon dioxide, with which the solution was in equilibrium; the gaseous concentration, as determined by analysis, multiplied by the coefficient of solubility, gave the concentration of the free acid in solution.

The same principle may be applied also to the study of solutions of salts of all non-volatile acids, provided they are sufficiently soluble both in water and in some inert solvent, which is immiscible with water, the aqueous solution, containing the acid and neutral salts, is shaken, until equilibrium is reached, with a solvent in which the acid is soluble but the salts insoluble. The concentration of the un-ionized free acid in the aqueous layer is directly proportional to the concentration of the same substance in the immiscible solvent, the proportionality factor being the partition coefficient of the free acid alone, for the two solvents. A simple analysis of the aqueous solution gives the remaining data for the calculation of the concentrations HX and X.

The aqueous solution of the acid and neutral salts of a dibasic acid, H_2X, will, in general, contain the following seven[2] molecular and ionic substances: NaHX, Na_2X, H_2X, Na, H, HX and X. If P is the partition coefficient, then H_2X, the molecular concentration of the un-ionized free acid, is equal to 0.5 P times the equivalent concentration of the ether solution. The relations between the concentrations of the six remaining substances may be expressed by six equations, as follows:

$$H \cdot HX = k_1 H_2X. \qquad (1)$$

If α_1 and α_2 are the degrees of ionization of the acid and neutral salts respectively, then, as close approximations,

[1] *Am. Chem. J.*, 29, 437 (1903).

[2] In moderately dilute solutions the amount of NaX ions is probably negligibly small.

$$HX = \alpha_1(NaHX + HX) \tag{4}$$

and

$$X = \alpha_2(Na_2X + X). \tag{5}$$

Since the solution is electrically neutral, we may write

$$Na + H = HX + 2X. \tag{6}$$

If the total concentration of the sodium is called m,

$$NaHX + 2Na_2X + Na = m. \tag{7}$$

Finally, if the equivalent acid concentration of the aqueous solution (as shown by the titration with standard alkali) minus P times the equivalent concentration of the ether solution be called C, we may write

$$NaHX + HX + H = C. \tag{8}$$

(4) and (5) give

$$HX = \alpha_1(C - H). \tag{9}$$

(1) and (9) give

$$HX = \frac{\alpha_1 C}{2} + \sqrt{\left(\frac{\alpha_1 C}{2}\right)^2 - k_1\alpha_1 H_2X}. \tag{10}$$

If H is very small compared with C, equation (9) becomes

$$HX = \alpha_1 C, \text{ nearly.} \tag{11}$$

Equation (10) also reduces to (11) if $k_1\alpha_1 H_2X$ is very small compared with $\left(\frac{\alpha_1 C}{2}\right)^2$.

(6) and (7) give

$$NaHX + 2Na_2X + HX + X - H = m. \tag{12}$$

(4), (5) and (12) give

$$\frac{HX}{\alpha_1} + \frac{2X}{\alpha_2} = m. \tag{13}$$

(9) and (13) give

$$X = \alpha_2\left[\frac{m + C}{2} - \frac{HX}{\alpha_1}\right]. \tag{14}$$

If $HX = \alpha_1 C$, equation (11),

$$X = \alpha_2\left(\frac{m - C}{2}\right). \tag{15}$$

Equations (10) and (14) must be used for highly ionized acids, like oxalic and dibromsuccinic, but the simplified forms (11) and (15) may be used, without appreciable error for weaker acids like succinic.

The following pages give an account of a few preliminary experiments made with salts of succinic acid, at 20°, using ether as the auxiliary solvent. The partition coefficient of succinic acid for water and ether was found by shaking an aqueous solution of pure succinic acid with carefully purified ether at a temperature of 20°, for a period of five minutes, a separate experiment having shown that equilibrium was reached

in that length of time. Forty cc. of the aqueous solution required 27.96 cc. of decinormal barium hydroxide, phenolphthalein being used as indicator. Forty cc. of ethereal layer, after evaporation of the ether and re-solution of the acid in water, required 3.78 cc. of the same barium hydroxide solution. The apparent partition coefficient is 27.96/3.78 = 7.40, but this must be corrected, since part of the acid in the aqueous solution is ionized, while that in the ethereal solution is not. The true partition coefficient is, as Nernst has shown[1] in all such cases, the ratio of the unionized portions of the acid in each solution. The aqueous solution was 4.28 per cent ionized, as calculated from its concentration, 0.0349 normal molecular, and the known ionization constant,[2] 66.5×10^{-6}. The true partition coefficient is, therefore, 7.40 (1 — 0.0428) = 7.08. Another aqueous solution of 0.1362 normal and therefore 2.19 per cent. ionized, gave for the partition coefficient 7.16 (1 — 0.0219) = 7.00. The mean of the two results, 7.04, is the true coefficient, which is independent of the concentrations of the solutions.

The details of a determination of the concentrations of the components of a solution containing both acid and neutral sodium succinate are illustrated by the following example: 20.00 cc. of exactly 0.2 molecular succinic acid and 20.00 cc. of exactly 0.25 normal sodium hydroxide were mixed with 50 cc. of purified ether and sufficient water so that after being shaken the volume of the aqueous solution would be approximately 50 cc. The mixture was then shaken vigorously for 5 or 6 minutes, at 20°, in a separatory funnel having three superimposed bulbs connected by short tubes, which were graduated. The two lower bulbs were each of 50 cc. capacity, while the upper bulb held about 150 cc. The two smaller bulbs and the connecting tubes were carefully calibrated. After being shaken, the solutions were allowed to settle. The volume of the ether was 50 cc.; that of the water solution was 50.42 cc.; therefore the sodium concentration, m, was $\frac{20 \times 0.25}{50.42} = 0.09916$. 20.00 cc. of the aqueous solution required 11.66 cc. of N/10 barium hydroxide; 40.00 cc. of the ethereal solution required 6.11 cc. of N/100 barium hydroxide. From these results it follows that the equivalent acid concentration of the aqueous solution was 0.05830, and that of the ethereal solution 0.001528. Therefore $C = 0.0583 - (7.04 \times 0.001528) = 0.04754$. If we take $\alpha_1 = 0.80$ and $\alpha_2 = 0.70$,[3] then $HX = \alpha_1 C = 0.03803$ and $X = 0.5\ \alpha_2\ (m - C) = 0.01807$. $H_2X = 0.5 \times 7.04 \times 0.001528 = 0.00538$.

These values substituted in equation (3) give $k_1/k_2 = 14.8$.

[1] *Z. physik. Chem.*, 8, 110 (1891).

[2] Ostwald: *Ibid.*, 3, 282 (1889).

[3] See following paper.

The results of seven experiments, of which the above calculation represents the fifth, are given in the following table:

	Molecular conc. H_2X.	Ionic conc. HX.	Ionic conc. X.	k_1/k_2.
1	0.01487	0.0520	0.0120	15.2
2	0.01258	0.0504	0.0129	15.7
3	0.01060	0.0480	0.0140	15.5
4	0.00862	0.0448	0.0152	15.3
5	0.00538	0.0380	0.0181	14.8
6	0.00276	0.0301	0.0218	15.1
7	0.00105	0.0208	0.0258	16.0
			Mean,	15.4

In all of the experiments represented by the above table the total sodium concentration was approximately N/10. For constant concentration of total base, the ratio k_1/k_2 is seen to be practically constant; $k_1 = 0.000,0665$, therefore $k_2 = 0.000,0043$. Further extensive measurements, using the method here delineated, have been carried out by Mr. Chandler, as described in the article following.

The secondary ionization constant of a dibasic acid, k_2, may be calculated very readily by a second new method from the conductivities of dilute solutions of the acid and neutral sodium salts. A. A. Noyes has shown[1] that, for a dilute solution (say N/1024) of the acid salt,

$$k_2 = \frac{(k_1 + m + H)H^2}{k_1(m - H)}. \qquad (16)$$

Of the quantities on the right-hand side of equation (16), m, the total concentration of the sodium is known, k_1 is also known; H, the concentration of free hydrogen ions, is the only unknown. This may also be found from relationships based upon the following considerations: For a very dilute solution of the pure acid-salt we may write

$$H\lambda_H + m\lambda_1 + HX\lambda_{HX} + X\lambda_X = m\Lambda_1 \qquad (17)$$

where λ_1 is the ionic conductivity of the univalent basic ion (sodium) and λ_H, λ_{HX} and λ_X the ionic conductivities indicated by the subscripts; Λ_1 is the observed molecular conductivity of the solution of the so-called acid salt; λ_1 is known and λ_X may be obtained from a single determination of the conductivity of a very dilute solution of the neutral salt.

It is obvious that λ_{HX} can not be determined in the ordinary way, on account of the formation of H and X ions from the acid salt, but the value of λ_{HX} may be calculated, in most cases, from the observed conductivity of the acid salt solution, when the ionic concentrations of the various sorts of ions have been determined by the equilibrium method already described; this would not, however, lead to an independent determination of k_2. It has already been clearly shown by Ostwald[2]

[1] *Z. physik. Chem.*, 11, 495 (1893).
[2] *Ibid.*, 2, 840 (1888).

and by Bredig[1] that ionic conductivity depends upon the composition of an ion, and that the conductivity may be very closely estimated from the composition. The values of λ_{HX} found in the two ways agree well. It has been observed, further, by Mr. Chandler,[2] that λ_{HX} is, in all cases, very nearly equal to $0.3\lambda_X$. If we accept this as a fixed relationship, the result will be at least a very close approximation. Therefore

$$\lambda_{HX} = 0.3\lambda_X. \tag{18}$$

For a very dilute solution of an acid sodium salt of a dibasic acid, it is easily seen[3] that

$$H_2X = X - H, \tag{19}$$

and

$$H_2X + HX + X = m. \tag{20}$$

(1), (19) and (20) give

$$X = \frac{(k_1 + m + H)H}{k_1 + 2H}; \tag{21}$$

(19) and (20) give

$$HX = m + H - 2X; \tag{22}$$

(17), (18), (21) and (22) give

$$H^2 - \frac{m(2\Lambda_1 - 2\lambda_1 - \lambda_X) - k_1(\lambda_H + 0.7\lambda_X)H}{2\lambda_H + \lambda_X} = \frac{k_1 m(\Lambda_1 - \lambda_1 - 0.3\lambda_X)}{2\lambda_H + \lambda_X}. \tag{23}$$

If

$$\frac{m(2\Lambda_1 - 2\lambda_1 - \lambda_X) - k_1(\lambda_H + 0.7\lambda_X)}{2(2\lambda_H + \lambda_X)} = a \tag{24}$$

and

$$\frac{k_1 m(\Lambda_1 - \lambda_1 - 0.3\lambda_X)}{2\lambda_H + \lambda_X} = b, \tag{25}$$

$$H = a + \sqrt{a^2 + b}. \tag{26}$$

Equations (24) and (25) may be simplified for sodium salts at the definite temperature, 25°, as follows. Let the concentration, m, $= \frac{1}{1024}$, and let Λ_2 be the equivalent conductivity of the salt Na_2X at this concentration, at which the equivalent conductivity due to the sodium ion is about 49.5. Therefore, $\lambda_1 = 49.5$ and $\lambda_X = 2(\Lambda_2 - 49.5)$. The value of λ_H is 352, at 25°, according to Kohlrausch and Steinwehr.[4] Substitution of these values in (24) and (25) gives

$$a = \frac{m(\Lambda_1 - \Lambda_2) - k_1(0.7\Lambda_2 + 141)}{2\Lambda_2 + 605} \tag{27}$$

and

[1] *Z. physik. chem.*, 13, 191 (1894).
[2] Next article.
[3] Equations (19) and (20) have been used by Noyes, *Loc. cit.*
[4] *Berl. Akad. Sitzber.*, 26, 570 (1902).

$$b = \frac{k_1 m(\Lambda_1 - 0.6\Lambda_2 - 20)}{2\Lambda_2 + 605}. \qquad (28)$$

In equation (26) the value of H is expressed in terms of quantities which are either known or easily determined experimentally, and, therefore, k_2 may now be obtained by substitution of the value of H, so found, in equation (16). The following application to the case of tartaric acid will serve as an illustration of the method, while numerous additional acids are similarly treated in Mr. Chandler's article. For tartaric acid, $k_1 = 970 \times 10^{-6}$;[1] if $m = \frac{1}{1024}$, $\Lambda_1 = 141$ and $\Lambda_2 = 108$. Therefore, $a = -2.167 \times 10^{-4}$, $c = +6.480 \times 10^{-8}$, $H = 117.6 \times 10^{-6}$ and $k_2 = 34.3 \times 10^{-6}$. The ratio $k_1/k_2 = 28.3$.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]

THE IONIZATION CONSTANTS OF THE SECOND HYDROGEN ION OF DIBASIC ACIDS.

BY E. E. CHANDLER.

Received March 3, 1908.

It is generally believed that dibasic acids ionize in two stages, thus:

$$H_2X \rightleftarrows H + HX \quad \text{and} \quad HX \rightleftarrows H + X.$$

From a study of the conductivities of dibasic acids, Ostwald[2] concluded that, excepting strong acids like oxalic, the second stage of the ionization did not take place to an appreciable extent at concentrations greater than milli-normal, since the primary ionization constant, k_1, as calculated from the relation,

$$H \cdot HX = k_1 \cdot H_2X, \qquad (1)$$

where the formulae H, HX, etc., represent molecular or ionic concentrations, was really a constant for all concentrations greater than 1/1024 normal. For smaller concentrations the apparent value of k_1 as calculated on the basis of equation (1) usually increased appreciably. This increase is the result of the ionization of the second hydrogen ion.

If the secondary ionization constant, *i. e.*, the ionization constant of the second hydrogen ion of a dibasic acid, is called k_2, then

$$H \cdot HX = k_2 \cdot HX. \qquad (2)$$

The magnitude of this constant has been determined previously for a considerable number of acids by four entirely different methods.

Trevor[3] determined the rate at which dilute solutions of acid salts of dibasic acids invert cane sugar, and from the results calculated the concentrations of the hydrogen ions in the solutions used. It was assumed

[1] Walden, *Z. physik. Chem.*, 8, 445 (1891).
[2] *Ibid.*, 3, 281 (1889).
[3] *Ibid.*, 10, 321 (1892).

that the dissociation of a salt like NaHX into Na and HX ions is practically complete in dilute solutions and that further ionization of the HX then yields H ions, the concentration of which governs the speed of inversion. A little later A. A. Noyes[1] developed a formula by means of which he calculated from Trevor's data the secondary ionization constants of the dibasic acids corresponding to the salts used by Trevor. Tower[2] found values approximating those of Trevor and Noyes by the use of oxidation cells. Smith[3] carefully repeated and extended Trevor's work, experiments being made to test the reliability of the method. Wegscheider[4] obtained secondary ionization constants from the conductivity of the free acids. A fourth, entirely distinct method was used by McCoy to find the secondary ionization constant of carbonic acid.[5] This method was later extended and applied to the study of succinic acid.[6] The method of McCoy as used for the latter acid, is based on the following considerations. It was shown that when an acid salt as NaHX, of a dibasic acid is dissolved in water it reacts thus:

$$2NaHX \rightleftarrows H_2X + Na_2X.$$

The state of equilibrium in such a solution, as well as in one containing any arbitrary ratio of total acid and base, is governed by the relations expressed by equations (1) and (2), which by combination give

$$\frac{HX^2}{H_2X \cdot X} = \frac{k_1}{k_2}. \qquad (3)$$

In order to determine the state of equilibrium one must know the concentrations of the components. To find the concentration H_2X the solution may be shaken, until equilibrium is reached, with an immiscible or partially miscible solvent, such as ether, in which the free acid is soluble, but the salt insoluble. The concentration of the acid in the ethereal layer, multiplied by a factor, which is a constant for a given acid at a fixed temperature, gives the concentration of the free acid, in molecular form, in the aqueous solution. This factor is the partition coefficient of the free acid for water and ether, which in this case is the ratio of the concentration of the molecular H_2X in an aqueous solution of the acid alone, to that of the total acid in an ethereal solution which is in equilibrium with the former. If the total concentration of the base, m, is known for the aqueous solution containing H_2X, NaHX and NaX, a determination of the total acidity, as shown by a titration, gives the remaining factor for the calculation of the concentrations of HX and X. The for-

[1] *Z. physik. Chem.*, 11, 495 (1893).
[2] *Ibid.*, 18, 17 (1895).
[3] *Ibid.*, 25, 144, 193 (1898).
[4] *Monatsh.*, 23, 599 (1902); 26, 1235 (1905).
[5] *Am. Chem. J.*, 29, 437 (1903).
[6] Preceding paper.

mulae by which these calculations are made are deduced in the preceding paper. It is there shown that in general

$$HX = \frac{\alpha_1 C}{2} + \sqrt{\left(\frac{\alpha_1 C}{2}\right)^2 - k_1 \alpha_1 H_2 X}, \tag{4}$$

and

$$X = \alpha_2 \left(\frac{m + C}{2} - \frac{HX}{\alpha_1}\right). \tag{5}$$

C is the equivalent acid concentration of the water solution minus P times the equivalent acid concentration of the ether solution; P is the partition coefficient; α_1 and α_2 are the degrees of ionization of the acid and neutral salts respectively, and k_1 is the primary ionization constant of the free dibasic acid; m is the total concentration of the base (say sodium) in the solution. In most cases these formulas may be greatly simplified; where $k_1 \alpha_1 H_2 X$ is very small compared with $\left(\frac{\alpha_1 C}{2}\right)^2$,

$$HX = \alpha_1 C \text{ nearly.} \tag{6}$$

In such cases

$$X = \alpha_2 \left(\frac{m - C}{2}\right). \tag{7}$$

The method just outlined was applied to the sodium salts of succinic acid by Professor McCoy, at whose suggestion I have studied the conditions of equilibrium in solutions of the salts of a number of other dibasic acids and from the results have calculated their secondary ionization constants. In the preceding paper it is shown how the secondary constants may also be calculated from the conductivities of the solutions of the acid and normal salts. I have also determined the conductivities of solutions of the salts of those acids studied by the partition method and from the results have obtained a set of independent values of the secondary ionization constants.

The experimental work described in the paper consists of three principal parts: the determination of

(1) The Partition Coefficients;
(2) The Equilibrium Constants;
(3) The Conductivities of the Salt Solutions.

I. The Partition Coefficients.

It is well known that a quantity of a substance shaken with a mixture of two immiscible or slightly miscible solvents at a fixed temperature is divided between the two in a constant ratio,[1] if the solute has the same molecular composition in the two solvents. If there is in either solvent partial dissociation or association of the solute, then it is found that a

[1] Berthelot and Jungfleisch, *Ann. chim. phys.* (4), 26, 396 (1874).

constant ratio of concentrations obtains only for those portions of the solute having the same molecular composition in the two solvents.[1]

This ratio is known as the partition coefficient. I have found ether to be the best solvent in general for use in the determination of the state of equilibrium in solutions of dibasic acids and their salts. The experiments of McCoy showed that the salts of succinic acid are not taken up by the ether. In most cases ether dissolves the acids satisfactorily and gives for aqueous solutions of the free acid a constant partition coefficient when allowance is made for ionization, thereby indicating that in the ethereal solution the acid exists in the simple molecular form. In other solvents, *i. e.*, chloroform, many acids are partially associated.[2] Moreover, an ethereal solution will readily separate from an aqueous solution, with which it has been shaken, while solutions of some of the other solvents tried do not readily do so. To purify the ether it was shaken with dilute sodium hydroxide solution, washed repeatedly with water, and finally distilled. The middle portion only was used. All of the partition coefficients were determined at 25° ±0.01, except one series at 0°. The substances were shaken together in a plain cork-stoppered bottle in a thermostat, first by a mechanical shaker, until they had come to the temperature of the bath, and then violently for a few minutes by hand and, finally, allowed to settle for about half an hour. This procedure was found sufficient to insure the attainment of equilibrium and to effect a complete separation of the ethereal and aqueous layers. In order to remove a sample of the aqueous solution unmixed with ether, the top stem of the pipette was closed by the moistened forefinger of one hand as the pipette was passed through the ether layer; the body of the pipette was then grasped in the other hand. Sufficient heat was thus communicated to expand the enclosed air and expel the drop or two of ether that had entered the stem of the pipette. The solutions were titrated with standard barium hydroxide, phenolphthalein being used as indicator. Before the titration of the ethereal solution, water was added and the ether distilled off. Most of the acids used were products of the firm of C. A. F. Kahlbaum.

The results of the partition experiments with the free acids are given in the tables of Series I. The first column gives the molar concentration, A, of the aqueous solutions after treatment with ether. The degree of ionization, α, of an acid was calculated from its primary ionization constant, k_1, by means of the equation

$$\frac{\alpha^2}{(1-\alpha)V} = k_1.$$

[1] Nernst, *Z. physik Chem.*, 8, 110 (1891). Hendrixson, *Z. anorg. Chem.*, 13, 73 (1897).

[2] Hendrixson, *Loc. cit.*

For oxalic and dibromsuccinic acids and for dilute solutions of maleic acid k_1 is not constant; for oxalic and maleic acids, α was obtained by interpolation from the results of Ostwald[1] and for dibromsuccinic acid from those of Walden.[2] The third column contains the values of the ratio, p, of the concentration of an aqueous solution of the acid to that of the corresponding ethereal solution. This ratio may be called the uncorrected partition coefficient. The true partition coefficient, P, is the ratio of the concentration of the unionized or molecular acid in the two solvents. It is easily seen that $P = p(1 - \alpha)$. The values contained in the last column are calculated from this relationship. All of the tables except one refer to partition between water and ether at 25° ±0.01. Table IV refers to succinic acid and these solvents at 0°.

Series I.—Partition Coefficients.

TABLE I.—OXALIC ACID.

$10^6 k_1 = 38000$.

A.	100 α.	p.	P.
0.3815	36	13.86	8.87
0.2767	42	15.44	8.84
0.2251	44	15.74	8.81
0.1911	46	16.35	8.83
0.1339	51	17.77	8.61
0.0887	60	21.66	8.64
0.0198	79	42.54	8.85
0.0103	86	61.38	8.35
0.0054	91.5	100.00	8.50
			8.64

TABLE II.—MALONIC ACID.

$10^6 k_1 = 1580$.

A.	100 α.	p.	P.
0.1478	9.8	10.94	9.86
0.1121	11.5	11.07	9.79
0.0862	12.6	11.28	9.86
0.0331	19.6	12.22	9.82
			9.83

TABLE III.—SUCCINIC ACID.

$10^6 k_1 = 66.5$.

A.	100 α.	p.	P.
0.1708	1.9	7.73	7.59
0.0582	3.2	7.79	7.54
0.0287	4.7	7.73	7.36
0.0217	5.4	7.81	7.39
0.0120	7.2	7.95	7.37
0.0059	10.0	8.39	7.55
0.0039	12.2	8.42	7.39
0.0023	15.6	8.79	7.42
			7 45

[1] *Z. physik. Chem.*, 3, 281 (1889).
[2] *Ibid.*, 8, 479 (1891).

TABLE IV.—SUCCINIC ACID AT 0°.

A.	100 *α*.	*p*.	*P*.
0.0705	3.0	4.43	4.30
0.0702	3.0	4.45	4.31
0.0374	4.1	4.43	4.25
0.0200	5.6	4.59	4.33
0.0126	7.0	4.64	4.32
0.0116	7.3	4.68	4.33
0.0063	9.8	4.67	4.21
0.0039	12.2	4.85	4.26
			4.30

TABLE V.—PIMELIC ACID.

$10^6 k_1 = 32.3$.

A.	100 *α*.	*p*.	*P*.
0.00998	5.54	0.7095	0.670
0.00702	6.56	0.7170	0.670
0.00480	7.87	0.7195	0.663
0.00284	11.30	0.7480	0.663
0.00179	12.60	0.7075	0.653
			0.664

TABLE VI.—GLUTARIC ACID.

$10^6 k_1 = 47.4$.

A.	100 *α*.	*p*.	*P*.
0.0280	4.0	3.72	3.57
0.0085	7.2	3.84	3.56
0.0072	7.8	3.91	3.60
0.0063	8.3	3.92	3.59
0.0056	8.9	3.93	3.58
			3.58

TABLE VII.—SUBERIC ACID.

$10^6 k_1 = 29.9$.

A.	100 *α*.	*p*.	*P*.
0.00986	5.3	0.215	0.204
0.00544	7.2	0.228	0.211
0.00175	12.2	0.246	0.216
0.00084	17.2	0.258	0.214
0.00049	21.9	0.274	0.214
			0.212

TABLE VIII.—AZELAIC ACID.

$10^6 k_1 = 25.3$.

A.	100 *α*.	*p*.	*P*.
0.00310	8.6	0.0679	0.0621
0.00178	11.2	0.0702	0.0623
0.00123	13.4	0.0718	0.0622
0.00096	15.0	0.0747	0.0635
0.00077	16.6	0.0753	0.0627
0.00064	18.0	0.0782	0.0641
0.00058	18.8	0.0800	0.0648
0.00051	19.9	0.0810	0.0649
0.00046	20.9	0.0823	0.0651
0.00033	24.1	0.0868	0.0659
			0.0637

TABLE IX.—SEBACIC ACID.

$10^6 k_1 = 23.8$.

A.	100 *α*.	*p*.	*P*.
0.00062	17.8	0.0213	0.0175
0.00058	18.3	0.0213	0.0174
0.00047	20.1	0.0221	0.0176
0.00036	22.6	0.0232	0.0179
			0.0176

TABLE X.—ORTHOPHTHALIC ACID.

$10^6 k_1 = 1210$.

A.	100 *α*.	*p*.	*P*.
0.0261	19.4	0.809	0.637
0.0197	21.9	0.822	0.642
0.0131	26.1	0.873	0.645
0.0119	27.2	0.894	0.651
0.0085	28.4	0.932	0.667
0.0057	36.7	0.996	0.631
0.0056	36.9	1.006	0.635
			0.644

TABLE XI.—METAPHTHALIC ACID.

$10^6 k_1 = 287$.

A.	100 *α*.	*p*.	*P*.
0.000398	56.2	0.0821	0.0359
0.000272	62.7	0.0943	0.0352
0.000263	62.9	0.0944	0.0350
0.000250	64.1	0.0949	0.0341
			0.0350

TABLE XII.—CAMPHORIC ACID.

$10^6 k_1 = 229$.

A.	100 *α*.	*p*.	*P*.
0.00229	9.5	0.0387	0.0350
0.00163	11.2	0.0398	0.0353
0.00148	11.7	0.0403	0.0357
			0.0353

TABLE XIII.—ITACONIC ACID.

$10^6 k_1 = 151.$

A.	100 *α.*	*p.*	*P.*
0.0615	4.8	2.99	2.83
0.0306	6.8	3.06	2.87
0.0161	9.2	3.18	2.88
0.0103	11.4	3.20	2.81
0.0091	13.8	3.22	2.83
0.0039	21.5	3.48	2.85
			2.86

TABLE XIV.—MALEIC ACID.

$10^6 k_1 = 11700.$

A.	100 *α.*	*p.*	*P.*
0.0993	29.0	9.60	6.82
0.0486	38.5	11.19	6.88
0.0337	44.1	12.20	6.82
0.0253	48.7	13.27	6.82
0.0196	53.0	14.40	6.78
0.0143	58.4	16.06	6.69
0.0100	63.7	17.78	6.45
0.0054	73.1	23.70	6.38
			6.71

TABLE XV.—FUMARIC ACID.

$10^6 k_1 = 930.$

A.	100 *α.*	*p.*	*P.*
0.0271	16.9	0.782	0.650
0.0114	24.8	0.871	0.655
0.0096	26.6	0.889	0.652
0.0092	27.1	0.893	0.648
0.0041	37.6	1.053	0.658
0.0041	37.6	1.040	0.650
			0.652

TABLE XVI.—MONOBROMSUCCINIC ACID.

$10^6 k_1 = 2780.$

A.	100 *α.*	*p.*	*P.*
0.0879	16.3	0.413	0.344
0.0283	26.8	0.479	0.352
0.0253	28.2	0.482	0.348
0.0131	36.7	0.599	0.380
0.0056	49.9	0.678	0.340
			0.345

TABLE XVII.—DIBROMSUCCINIC ACID.

$10^6 k_1 = 34000.$

A.	100 *α.*	*p.*	*P.*
0.0327	67.6	0.0578	0.0187
0.0307	68.6	0.0595	0.0187
0.0302	69.1	0.0603	0.0186
			0.0187

The results found for oxalic acid are remarkable; while the value of p increases more than sevenfold within the range of concentrations used the value of P is so nearly constant that the variations may reasonably be considered as due to experimental errors. Now the value of α used in calculating P by means of the equation $P = p\,(1 - \alpha)$ is that determined from the conductivity of the acid. In its change of ionization with change of concentration, oxalic acid does not follow exactly the Ostwald dilution law, in which respect it resembles salts and the stronger acids and bases. One of the most important problems connected with the ionic theory has been to decide whether the degree of ionization as determined in the ordinary way from the results of conductivity measurements of a good electrolyte is correct. Assuming the validity of the partition law, the constancy of the value of P seems clearly to indicate the accuracy of the values of α used. The view that the correct value of α is given by conductivity measurements is in accord with the conclusion of A. A. Noyes, who has subjected all the other evidence on this point to a critical review.[1] The constancy of the partition coefficient, P, is equally good for the balance of the acids, for most of which the dilution law holds true.

II. Equilibrium in Solutions of Salts of Dibasic Acids; Determination of Equilibrium Constants.

It has been shown that the state of equilibrium in a solution containing neutral salt, acid salt and free dibasic acid is represented by the equation

$$\frac{HX^2}{H_2X \cdot X} = \frac{k_1}{k_2}. \qquad (3)$$

The methods of determining the concentration of each of the constituents of such a solution was outlined in the introduction. In order to calculate the total concentration of the basic ion it is necessary to know the final volume of the aqueous solution. When water is shaken with ether, previously saturated with water, the volume of the aqueous layer increases; this increase in volume was in some cases measured directly in the manner indicated by McCoy for succinic solutions. In most experiments, however, it was found more convenient to determine the increase in volume in another way. It was found by experiment that when water or a dilute solution, such as was used in these experiments, was shaken with ether previously saturated with water, that the increase in volume of the aqueous solution always amounted, at 25°, to 7.8 per cent., and at 0°, to 15 per cent. The details of the experimental procedure for the determination of the equilibrium constant may be illustrated by an example taken from the work of glutaric acid. A quantity of pure glutaric acid sufficient to give a mixture of the acid and neu-

[1] International Congress, St. Louis, 1904, Vol. IV, p. 311.

tral salts was added to 25.00 cc. of exactly normal sodium hydroxide and the solution diluted to 250 cc. Exactly 20 cc. of the resulting solution were shaken in a plain 250 cc. bottle with about 75 cc. of ether at a temperature of 25° ±0.01 until equilibrium was reached. This occurred within ten minutes. After the solution had stood in the thermostat for about thirty minutes longer and the ether and the aqueous layers had completely separated, a portion of each was removed, in the manner described for the determination of the partition coefficients, and titrated with standard barium hydroxide, the ether solution being first evaporated after the addition of water. In all cases phenolphthalein was used as indicator. 20 cc. of the aqueous solution required 10.70 cc. of 0.0972 normal barium hydroxide; 50 cc. of the ether solution required 18.60 cc. of 0.00992 normal barium hydroxide. Therefore the (equivalent) acid concentration of the aqueous solution $= \frac{10.70 \times 0.0972}{20} =$ 0.0520, and the (equivalent) acid concentration of the ethereal solution $= \frac{18.60 \times 0.00992}{50} = 0.00369$.

$$C = 0.0520 - 3.58 \times 0.00369 = 0.0388.$$
$$H_2X = 0.5 \times 3.58 \times 0.00369 = 0.0066.$$

Since the aqueous volume is increased 7.8 per cent. by the absorption of ether, the total concentration of the sodium $= m = 0.1/1.078 =$ 0.0928. HX and X may be calculated by the simplified formulas: $HX = \alpha_1 C$, and $X = \alpha_2\left(\frac{m-C}{2}\right)$. $\alpha_1 = 0.79$ and $\alpha_2 = 0.70$. Therefore, $HX = 0.0306$ and $X = 0.0189$.

$$\frac{k_1}{k_2} = \frac{HX^2}{H_2X \cdot X} = 7.50.$$

$$10^6 k_1 = 47. \quad \text{Therefore, } 10^6 k_2 = 6.3.$$

Since the sodium salts of monobasic acids are, in general, very nearly equally ionized at equal concentrations, it seems probable that the tendency of an acid salt, NaHX, to ionize into Na and HX must be about the same as that of the simpler salts, NaX. Consequently it has been assumed that α_1, the degree of ionization of NaHX, is equal to that of sodium acetate at the same concentration. The degree or ionization, α_2, of a normal salt Na_2X has been taken the same as that of normal sodium succinate at the same concentration. The equilibrium concentrations have been determined for solutions of the sodium salts of all the acids in Series I with the exception of oxalic, in which case the potassium salts were used on account of their greater solubility in water. Some difficulties were encountered in certain cases. The aqueous solution of potassium acid oxalate contains but a very small proportion of free acid and

neutral salt. This condition is unfavorable for an accurate determination of the equilibrium concentrations and therefore of the ratio k_1/k_2. The same kind of difficulty in still greater degree appeared in the study of maleic acid solutions. It was necessary in each case to use a proportionately large quantity of the ether solution to obtain an accurate titration. Mono- and dibromsuccinic acids also present difficulties in that each is acted upon slowly by water, the first to give hydrobromic and malic acids,[1] and the second to give hydrobromic and brommaleic acids.[2] However, the action of water at 25° is too slow to cause very appreciable errors.

TABLE XVIII.—GLUTARIC ACID

α_1.	α_2.	m.	C.	H_2X.	HX.	X.	k_1/k_2.	k_1/k_2.
0.75	0.64	0.1855	0.0808	0.0167	0.0606	0.0335	6.6	
0.75	0.64	0.1855	0.0807	0.0170	0.0605	0.0335	6.4	6.5
0.78	0.695	0.1022	0.0405	0 0068	0.0316	0.0214	6.8	
0.78	0.695	0.1022	0.0437	0.0089	0.0341	0.0203	6.4	
0.78	0.695	0.1022	0.0448	0.0090	0.0349	0.0200	6.8	6 7
0.79	0.70	0.0936	0.0464	0.0114	0.0366	0.0165	7.1	
0.79	0.70	0.0936	0.0528	0.0165	0.0417	0.0143	7.4	
0.79	0.70	0.0936	0.0529	0.0165	0.0418	0.0142	7.4	
0.79	0.70	0.0936	0.0480	0.0119	0.0379	0.0160	7.6	7.4
0.79	0.70	0.0928	0.0388	0.0066	0.0306	0.0189	7.5	
0 79	0.70	0.0928	0.0464	0.0113	0.0366	0.0162	7.3	7.4
0.81	0.73	0.0618	0.0084	0.0025	0.0068	0.0195	9.5	
0.81	0.73	0.0618	0.0164	0.0151	0.0133	0.0166	7.1	
0.81	0.73	0.0618	0.0269	0.0489	0.0218	0.0127	7.6	
0.81	0.73	0.0618	0.0316	0.0763	0.0256	0.0110	7.6	
0.81	0.73	0.0618	0.0344	0.0445	0.0279	0.0100	8.2	
0.81	0.73	0.0618	0.0406	0.0150	0.0329	0.0077	9.4	8.1
0.83	0.76	0.0464	0.0254	0.0064	0.0211	0.0080	8.7	
0.83	0.76	0.0464	0.0261	0.0068	0.0217	0.0077	8.9	
0.83	0.76	0.0464	0.0248	0.0070	0.0206	0.0082	7.4	
0.83	0.76	0.0464	0.0248	0.0067	0.0206	0.0082	7.7	
0.83	0.76	0.0464	0.0252	0.0068	0.0209	0.0081	8.0	8.2
0.84	0.77	0.0366	0.0199	0.00526	0.0167	0.00643	8.3	
0.84	0.77	0.0362	0.0197	0.00514	0.0165	0.00635	8.4	
0.85	0.87	0.0316	0.0172	0.00490	0.0146	0.0562	7.8	
0.85	0.87	0.0309	0.0172	0.00490	0.0146	0.00534	8.2	8.2
0.90	0.83	0.0155	0.0083	0.00204	0.0075	0.00299	9.1	
0.90	0.83	0.0155	0.0086	0.00236	0.0077	0.00286	8.9	9.0

Table XVIII gives the details of all experiments with glutaric acid. The symbols m, C, HX, and X represent the respective concentrations in terms of gram *equivalents* per liter, while H_2X refers to gram *molecules* per liter. The simpler formulae, (6) and (7), have been used for calculating HX and X in all cases, except for oxalic and dibromsuccinic

[1] Tantor, *J. Russ. Chem. Soc.*, **23**, 339 (1892). Beilstein, *Org. Chem.*, **1**, 658.
[2] Van't Hoff, *Études de Dyn. Chem. Amsterdam*, page 14.

acids. Table XIX gives, in condensed form, the results for other acids; in each case several determinations were made at each concentration, as in the case of glutaric acid. The details are omitted in order to save space.

TABLE XIX.

RATIO OF IONIZATION CONSTANTS, k_1/k_2, AT VARIOUS CONCENTRATIONS, m.

Oxalic.....	m	0.2691	0.1346	0.0769	0.0598	0.0448	0.0245		
	k_1/k_2	871	981	919	840	1087	880		
Malonic.....	m	0.3134	0.1880	0.1180	0.0940	0.0784	0.0587	0.0470	0.0393
	k_1/k_2	357	390	444	459	474	470	488	493
Succinic.....	m	0.1870	0.0834	0.0312	0.0170	0.0046			
	k_1/k_2	15.5	16.9	19.2	21.0	26.6			
Glutaric.....	m	0.1855	0.1022	0.0936	0.0618	0.0464	0.0362	0.0155	
	k_1/k_2	6.5	6.7	7.4	8.1	8.2	8.4	9.0	
Suberic.....	m	0.1855	0.0824	0.0311	0.0169				
	k_1/k_2	4.2	4.7	5.4	6.1				
Pimelic.....	m	0.1859	0.0833	0.0309	0.0169				
	k_1/k_2	3.9	4.4	5.2	5.6				
Azelaic.....	m	0.1855	0.0824	0.0311	0.0169				
	k_1/k_2	4 2	4.8	5.2	5.8				
Sebacic.....	m	0.1855	0.0824	0.0337	0.0169	0.0046	0.0018	0.00092	0.00046
	k_1/k_2	4.0	4.2	4.8	5.7	7.4	9.1	9.2	10.4
o-Phthalic....	m	0.1858	0.0825	0.0309	0.0170	0.0089			
	k_1/k_2	165	200	240	265	290			
m-Phthalic...	m	0.0926	0.0463	0.0311					
	k_1/k_2	5.3	6.6	6.5					
Camphoric...	m	0.0923	0.0461	0.0154	0.0084				
	k_1/k_2	8.1	9.3	11.3	13.2				
Itaconic.....	m	0.0926	0.0468	0.0156	0.0084				
	k_1/k_2	33.7	38.9	46.1	57.0				
Maleic.....	m	0.0926							
	k_1/k_2	30000							
Fumaric.....	m	0.0926	0.0468	0.0156	0.0084				
	k_1/k_2	18.3	20.3	25.8	30.0				
Monobrom-succinic....	m	0.0926	0.0463	0.0156	0.0084				
	k_1/k_2	46.0	54.0	69.0	91.0				
Dibromsuc-cinic.....	m	0.0927	0.0463	0.0157					
	k_1/k_2	10.9	13.5	12.6					

In discussing the results we may consider the influence of three factors upon the value of the equilibrium constant: (1) The effect of the ratio of the total base to the total acid in solutions of the salts where the concentration of the base is constant; (2) The effect of the total concentration of the base; (3) The effect of temperature. The experiments of McCoy on carbonates and succinates showed that, for constant concentra-

tions of the total base, the value of k_1/k_2 is independent of the ratio of base to acid. My experiments lead to the same conclusion. If an aqueous solution of the pure acid salt (that is, one having equal molecular concentrations of base and acid) is shaken with ether the ratio of base to acid becomes greater than unity. In the experiments here described no attempt was made to maintain equal concentrations of base and acid in the aqueous solution; indeed in the case of glutaric acid the ratio was varied greatly in order to test the independence of k_1/k_2. The ratio of total base, m, to total acid in any experiment, is $\frac{m}{\frac{C+m}{2}+H_2X}$. In the seventh experiment with glutaric acid this ratio is 1.044; in the tenth it is 1.282; and in the twelfth it is 1.644. Such a high value of the ratio as the last is unfavorable to accuracy because of the exceedingly small titer of the ether solution; this doubtless accounts for the abnormal value found for k_1/k_2.

On the other hand, in the seventeenth experiment the ratio is 0.735 and it is interesting to note that in spite of the large excess of acid above that required to form the dry acid salt the solution contains an appreciable amount of the ion of the neutral salt. Here the great excess of acid is also unfavorable for an accurate determination of the constant; nevertheless, the value found is not far from the mean. In the first experiment with a sebacic acid the ratio of base to acid is 1.84. Owing to the limited solubility of the acid in water, it is impossible to decrease this ratio very much at large concentrations of the base. Sebacic acid, however, is so much more soluble in ether than in water that there is always sufficient acid in the ether solution to make an accurate titration possible and no difficulty was found in getting concordant values of k_1/k_2.

I have found that k_1/k_2 increases with decreasing concentration of the total base. A similar result was found by McCoy for carbonates. Smith also observed a diminishing value of k_2 with dilution. This is equivalent to an increase of k_1/k_2 if k_1 is constant.

The values of k_1/k_2 have been found by inter- and extrapolation for the concentrations 0.1, 0.01 and 0.001 of total base with results shown in the following table. The last two columns contain the ionization constants of the first and second hydrogen ions. The values of k_2 were calculated from those of k_1/k_2 for 0.001 normal concentration:

TABLE XX.

	k_1/k_2.				
	Conc. 0.1.	Conc. 0.01.	Conc. 0.001.	10^6k_1.	10^6k_2.
Oxalic	930.0	930	930	38000	40.9
Malonic	460	610	780	1580	2.03
Succinic	16.5	23.5	30.5	66.5	2.18
Glutaric	7.0	9.8	14.0	47.4	3.38

TABLE XX (*Continued*).

	Conc. 0.1.	Conc. 0.01.	Conc. 0.001.	10^6k_1.	10^6k_2.
Suberic	4.6	6.4	8.1	29.9	3.67
Pimelic	4.4	5.9	7.4	32.3	4.37
Azelaic	4.6	6.1	7.6	25.3	3.33
Sebacic	4.1	6.5	9.2	23.8	2.59
o-Phthalic	190	290	390	1210	3.10
m-Phthalic	5.2	8.1	10.8	287	26.6
Camphoric	8.0	12.4	16.4	229	14.0
Itaconic	32.0	51	70	151	2.16
Maleic	30000	(45000)	(60000)	11700	0.20
Fumaric	17.0	30	43	930	21.6
Monobromsuccinic	44.0	78	112	2780	24.8
Dibromsuccinic	10	(16)	(22)	34000	1540

The values in parentheses, for maleic and dibromsuccinic acids, are uncertain.

The effect of temperature was determined by means of a series of experiments at 0° with succinates. The following results were obtained:

TABLE XXI.

m	0.1739	0.0869	0.0497	0.0290	0.0158
k_1/k_2	15.5	16.7	18.0	19.7	23.1

It will be seen that although the partition coefficient of succinic acid at 0° (fourth table, Series I) is 4.30, instead of 7.45 at 25°, yet the value of k_1/k_2 is practically the same at the two temperatures. This fact is in accord with many well-known results, which show that degrees of ionization and ionization constants are, for most substances, nearly the same at 0° and at 25°.

It is interesting to note that k_1/k_2 for the dibromsuccinic acid is not greatly different from k_1/k_2 for succinic acid, although both k_1 and k_2 are enormously greater. Halogen substitution has therefore affected the dissociation of the two hydrogens about equally.

A series of experiments was carried out with sebacic acid, using chloroform instead of ether. The results of the partition experiments, conducted at 25° ± 0.01 are given in the following table. A_w and A_c represent the molecular concentrations of the acid in the water and chloroform solutions respectively. It is well known that there is association of the molecules of many substances when dissolved in chloroform. Allowance for α only, therefore, fails to make the values of P constant. The smaller values of P for the more concentrated solutions indicate, of course, a greater degree of association in the chloroform.

TABLE XXII.—PARTITION COEFFICIENTS OF SEBACIC ACID.

A_w.	A_c	α.	p.	P.
0.00100	0.000963	14.3	1.04	0.89
0.00059	0.000438	18.2	1.36	1.09
0.00030	0.000176	24.5	1.70	1.29
0.00018	0.000087	30.3	2.08	1.45

The following table contains the results obtained in the determination of k_1/k_2 for sebacic acid by the chloroform method. The column headings have the same significance as in the tables where ether was used, but the column headed A_c gives in addition the concentration of the acid in the chloroform. The experimental treatment is the same as that described for ether extraction except in two particulars. (1) The solubility of chloroform in water is so slight that the volume of the water solution is not changed when it is mixed with chloroform, so that the concentration of the total base is not altered thereby. (2) Inasmuch as there is no constant partition coefficient, its value for each experiment with a salt solution usually must be determined by interpolation. No partition experiment was made with the free sebacic acid in which the chloroform concentration was so great as that of the first experiment of the following table. The corresponding value of P, 0.84, was obtained by graphical extrapolation:

TABLE XXIII.—SEBACIC ACID.

α_1.	α_2.	m.	C.	A_c.	P.	H_2X.	HX.	X.	k_1/k_2.
0.73	0.63	0.20080	0.02104	0.00148	0.84	0.00125	0.0154	0.0566	3.33
0.79	0.70	0.09245	0.01182	0.00085	0.91	0.00077	0.0093	0.0282	4.01
0.79	0.70	0.09245	0.01195	0.00094	0.89	0.00083	0.0094	0.0282	3.79
0.85	0.78	0.03346	0.00454	0.00026	1.17	0.00031	0.0039	0.0113	4.34
0.85	0.78	0.03346	0.00484	0.00033	1.14	0.00038	0.0041	0.0112	3.95
0.88	0.82	0.01826	0.00269	0.00016	1.30	0.00021	0.0024	0.0064	4.29
0.88	0.82	0.01826	0.00253	0.00014	1.33	0.00019	0.0022	0.0065	3.92

The first value of k_1/k_2 is uncertain on account of the uncertainty of the factor $P = 0.84$. The remaining values of k_1/k_2 are almost constant. However, too much stress should not be laid on the constancy, as the method is involved by the phenomenon of association.

For an acid which is difficulty soluble in water, k_1/k_2 may be determined in a manner still different from that described above. The solubility of the acid in pure water is first determined and allowance made for dissociation in the usual way. When the solid acid is present in excess the concentration of the undissociated portion of the dissolved acid in aqueous solution of the free acid is equal to its concentration when the salts also are present. It is well known that it is not easy to determine with accuracy the solubility of a difficultly soluble substance. About two months were spent in an endeavor to find the solubility of sebacic acid in water. Equilibrium between the dissolved and undissolved acid was sought by approaching 25° from both a higher and a lower temperature. Rapid shaking was found to increase the solubility considerably. The result is probably to be explained by the comminution of the crystals by the greater agitation, it being apparently well established that smaller particles are more soluble than larger ones.[1] Forty-four ex-

[1] Ostwald, *Z. phys. Chem.*, **34**, 495 (1900); Hulett, *Ibid.*, **37**, 385 (1901).

periments gave an average molar concentration of 0.00118; individual values ranged from 0.00125 to 0.00105. At a molar concentration of 0.00118, the degree of dissociation is 13.3 per cent. Therefore the concentration of the undissociated portion is 0.00118 × 0.867 = 0.0010. To filter the solution, it was drawn into a pipette by means of a filter pump through a closely packed cotton plug. It was then titrated. That error did not arise from imperfect filtration was shown by the fact that separately filtered portions of the same solution had the same concentrations.

To determine k_1/k_2 sodium hydroxide of known concentration was shaken with excess of acid, filtered as described, and titrated. The factors of equation (3) are determined in the same manner as for the partition method, except that the concentration, H_2X, remains 0.0010 for all experiments. This method of determining k_2/k_2 for sebacic acid was not satisfactory. It was even more difficult to get a constant equilibrium between the acid salt, the neutral salt, the dissolved and undissolved acid, than between the last two alone.

The values found for k_1/k_2 averaged about 5, but some values more than double this amount were found without my being able to assign any reason therefor.

The same method was also tried with suberic acid, but only one experiment was made. The molar concentration of its saturated solution was found to be 0.0144, at which concentration the degree of dissociation is 4.4 per cent. and the molar concentration of the undissociated acid is 0.0138. In a single experiment in which the total concentration of sodium was 0.201 the value 5.5 was found for k_1/k_2 for suberic acid. It is possible that an acid of about this solubility would give constant results and regret is expressed that more experiments were not made with suberic acid by this method.

III. The Determination of the Secondary Ionization Constant of a Dibasic Acid by the Conductivity Method.

The conductivity of the negative ion, HX, of an acid salt, NaHX, cannot be found in the usual way on account of the ionic interactions of the solution of the acid salt. The values used by Ostwald[1] and Bredig[2] as the conductivities of HX ions, for the calculation of the degrees of ionization, from the conductivities of the free dibasic acids, were merely estimated from the composition of the ion.

I have found the approximate values of such ionic conductivities in the following manner: The concentrations of acid and neutral salts

[1] *Z. phys. Chem.*, **2**, 840 (1888); **3**, 281 (1889).
[2] *Ibid.*, **13**, 191 (1894).

and of free H ions were calculated for a dilute solution, say N/1000, of the pure acid salt, by means of the value k_1/k_2 found by partition experiments. The observed equivalent conductivity of the solution of the acid salt diminished by the conductivity due to the neutral salt and H ions represents the conductivity of the ions of the acid salt. This difference, by division of a number representing the fraction of the sodium actually in the form of acid salt gave the true (hypothetical) equivalent conductivity of the acid salt. By subtracting from the latter value the known ionic conductivity of sodium the ionic conductivity of HX remained.

The results so obtained clearly revealed a very simple relationship. *The conductivities of the HX ions were all approximately proportional to those of the corresponding X ions.* The detailed results of these calculations are omitted, but the relationship discovered has been utilized to calculate the secondary ionization constants by a method entirely independent of the data of the partition experiments. The good agreement between the values of k_2 as found by the partition and conductivity methods serves, of course, as an equally satisfactory test of the accuracy of the law just announced.

The same relationship between the conductivities of HX and X was observed when the conductivities of the HX ions were estimated in another way. The work of Ostwald[1] and Bredig[1] has served to show that the conductivity of an organic ion is dependent upon its composition. Univalent, isomeric ions are equally mobile, and univalent ions, composed of the same number of atoms, have practically the same conductivity. One may therefore safely assume that the conductivity of any ion, HX, of a dibasic acid, H_2X, is equal to that of an ion of the most nearly related monobasic acid. Thus the conductivity of the acid succinic ion, $HCO_2.CH_2.CH_2.CO_2$, may be considered equal to that of the ion of butyric acid, $CH_3.CH_2.CH_2.CO_2$.

In Table XXIV, $\frac{1}{2}\lambda_X$ is the *equivalent* conductivity of the X ion of the corresponding dibasic acid; λ is the equivalent conductivity of the negative ion of that monobasic acid most closely resembling the dibasic acid of the same line. The ratio, $\lambda/\frac{1}{2}\lambda_X$, is nearly a constant, the mean value of which is 0.595; or practically 0.6. We may therefore consider that

$$\lambda_{HX} = 0.6 \times \tfrac{1}{2}\lambda_X = 0.3\lambda_X. \qquad (8)$$

It is readily seen that the value of λ_{HX}, last column, Table XXIV, calculated by this equation, does not differ greatly, in any case, from that of λ.

[1] *Loc. cit.*

TABLE XXIV.

	$\frac{1}{2}\lambda_X$.		λ.	$\lambda/\frac{1}{2}\lambda_X$.	$0.3\lambda_X=\lambda_{HX}$.
Oxalic	72.4	Acetic	41.6	0.575	43.4
Malonic	64.1	Propionic	36.8	0.574	38.5
Succinic	56.0	Butyric	33.0	0.589	33.6
Glutaric	51.0	Valerianic	31.0	0.608	30.6
Suberic	44.3	Phthaluric	26.5	0.598	26.5
Azelaic	43.3	Phthalanilic	26.2	0.605	26.0
Sebacic	40.1				24.1
Camphoric	40.8				24.5
o-Phthalic	49.8	Toluic	32.1	0.651	29.9
m-Phthalic	50.0	"	32.1	0.642	30.0
Itaconic	55.7	Angelic	31.5	0.566	33.4
Maleic	60.0	Crotonic	34.5	0.575	36.0
Fumaric	60.6	"	34.5	0.569	36.4
Monobromsuccinic	56.4	Butyric	33.0	0.585	33.8
Dibromsuccinic	55.2	"	33.0	0.598	33.1
			Mean,	0.595	

By means of the relationship just discussed, McCoy has shown in the preceding paper, how the concentration of hydrogen ions in the solution of an acid salt of a dibasic acid may be calculated from conductivity data. For the acid sodium salt of N/1024 concentration,

$$H = a + \sqrt{a^2 + b} \qquad (9),$$

where

$$a = m\frac{(\Lambda_1 - \Lambda_2) - k_1(0.7\,\Lambda_2 + 141)}{2\Lambda_2 + 605} \qquad (10)$$

and

$$b = \frac{k_1 m(\Lambda_1 - 0.6\,\Lambda_2 - 20)}{2\Lambda_2 + 605} \qquad (11)$$

and Λ_1 and Λ_2 represent the observed equivalent conductivities of the acid and normal salts respectively, at 25° and N/1024 concentration. The value of H calculated by means of the preceding equations may be used to calculate k_2 by substitution in Noyes's equation:[1]

$$k_2 = \frac{(k_1 + m + H)H^2}{k_1(m - H)}. \qquad (12)$$

I have measured the conductivities of those acid and normal salts studied by the partition method. The results are given in Tables XXV and XXVI. The conductivities of the acid salts of oxalic and malonic acids, as well as of many of the neutral salts, have been measured previously by Walden[2] and Bredig.[3] My results agree well in general with those of Walden and Bredig, in so far as comparison is possible.

[1] *Z. phys. Chem.*, 11, 495 (1893).
[2] *Ibid.*, 8, 433 (1891).
[3] *Ibid.*, 13, 191 (1894).

TABLE XXV.—CONDUCTIVITIES AT 25° IN RECIPROCAL OHMS OF ACID SALTS—NaHX

Dilution.	32.	64.	128.	256.	512.	1024.	2048.	4096.
Oxalic	97	109	123	139	158	182	211	250
Malonic	80.5	84	87	90.6	97.3	104.8	113	126
Succinic	76	80	83.3	86.5	89.5	94	101	111
Glutaric	73.4	78.7	82.4	85	88	91.6	98	106.4
Suberic	68.9	72.5	75.7	78.3	81.5	85	91	99
Azelaic	68.9	72.5	75.7	79.3	81.5	85	89.8	97
Sebacic			75	78	80	82.9	88.3	95
o-Phthalic	70.6	75	80	85	92	100	112	125
m-Phthalic				91.3	100.6	115	136	171
Itaconic	74	77.8	81.4	85.2	89	94.8	102.6	116
Maleic	79	84	88	91.5	95	99.5	104	110
Fumaric	80.5	86.2	93	104	118.7	140	170	205
Monobromsuccinic	78.6	86	96.5	109	127	151	180.6	217
Dibromsuccinic	150	187	231	280	331	381	422	456

TABLE XXVI.—NORMAL SALTS—Na_2X.

Dilution.	32.	64.	128.	256.	512.	1024.	2048.	4096.
Oxalic	99	105	110	115	118	120	121	122
Malonic	91.7	98.2	102.4	105.5	109	112	114	115.5
Succinic	87.3	92.3	96.7	99.7	102	104	105.5	106
Glutaric	82.9	88.2	92.5	95	97	99	101	102
Suberic	76	81.4	85.3	88.1	90.6	92.3	94.5	96
Azelaic	75	80	84	87	89	91	92	93
Sebacic			81	84	86.4	88	90	91
o-Phthalic	81.5	86.5	91	94	96	98	99	100
m-Phthalic				92	95	98	101	105
Itaconic	86	90.6	95	98.4	102	104	105	106
Maleic	90	95	99	102.5	105.5	108	109	109.5
Fumaric	89.5	94.6	98.5	102	105	108	110	112
Monobromsuccinic	86	91	95	99	102	105	108	112
Dibromsuccinic	84	89	94	98	101	104	107	110

Table XXVII gives the results calculated from these conductivities by equations (9) and (12):

TABLE XXVII.

	Λ_1.	Λ_2.	10^8k_1.	10^6H.	10^6k_2.
Oxalic	182	120	38000	193	49
Malonic	104.8	112	1580	35	2.1
Succinic	94	104	66.5	12.9	2.7
Glutaric	91.6	99	47.4	11.4	2.9
Suberic	85	92.3	29.9	7.4	1.9
Azelaic	85	91	25.3	7.7	24.
Sebacic	82.9	88	23.8	7.6	2.5
o-Phthalic	100	98	1210	44.4	3.9
m-Phthalic	115	98	287	67.9	24.
Itaconic	94.8	104	151	18.7	2.8
Maleic	99.5	108	11700	15.1	0.26
Fumaric	140	108	930	113	32
Monobromsuccinic	151	105	2780	151	39
Dibromsuccinic	381	104	34000	675	1600

Table XXVIII contains all of the values which I have found for the ionization constants of the second hydrogen ion of the dibasic acids studied, together with those found by Smith, Wegscheider and Trevor.

TABLE XXVIII.—SECONDARY IONIZATION CONSTANTS, $10^8 k_2$.

	Partition.	Conductivity.	Smith.	Wegscheider.	Trevor.
Oxalic	41	49	..	..	16.0
Malonic	2.0	2.1	1.0	10	..
Succinic	2.2	2.7	2.3	..	..
Glutaric	3.4	2.9	2.7	..	..
Suberic	3.7	1.9	2.5	3.3	..
Pimelic	4.4	..	..	..	..
Azelaic	3.3	2.4	2.7	..	..
Sebacic	2.6	2.5	2.6	..	..
o-Phthalic	3.1	3.9	1.7	..	..
m-Phthalic	27	24	..	..	10.0
Camphoric	14	..	0.7	..	..
Itaconic	2.2	2.8	2.3	..	..
Maleic	0.20	0.26	0.4	8.0	..
Fumaric	22	32	18	29	..
Monobromsuccinic	25	39	..	39	..
Dibromsuccinic	1540	1600	..	..	..

The methods of Trevor and Smith are similar, except that a different constant is used for the inversion effect of a completely dissociated acid. Their solutions were 1/128 normal with respect to the acid salts and the experiments were carried out at 100°, as the speed of inversion was too slow at 25°. This should not materially effect the value of k_2, unless there was some decomposition of the acid at high temperature. Smith found that malonic acid suffered decided decomposition at 100° and the value given is an interpolation. He also found that a neutral salt or even water caused quite as rapid an inversion as an acid salt, although in the former cases the rate was irregular. From these considerations, it is remarkable that values obtained by Smith's method agree so well with others.

The method of Wegscheider, using the free acid, is probably less accurate than the method using the acid salt. Even though the latter is complicated by the presence of the neutral salt. The former method is evidently more accurate for acids having a large value of k_2 than for those for which k_2 is small. The values found by Wegscheider for suberic, fumaric and monobromsuccinic acids agree very well with those I have found. But his values of k_2 for maleic and malonic acids, which other experimenters find to be small, are certainly too large.

In conclusion, I wish to express my obligation to Dr. McCoy, under whose supervision the foregoing work has been carried out.

ON THE FREE ENERGY OF NICKEL CHLORIDE.

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1. Introduction.

In a previous paper[1] by one of the authors, calculations of the free energy have been made, from potential measurements, of all compounds for which the necessary data already existed, but so far no direct free energy determinations of salts have been made on the principle underlying these computations. The object of the following investigation is to determine the free energy of nickel chloride by this method, for a full description of which reference may be made to the above paper. Briefly, for the salt here investigated it consists in measuring the electromotive force of the cell:

$$\text{Nickel} \mid \text{Saturated sol. of } NiCl_2 \mid Pt + Cl_2.$$

If the salt contained no water of crystallization and the chlorine were at a pressure of 76.0 cm. of mercury the free energy increase of one mol of the salt would be

$$\Delta F = -2EF$$

where E is the measured electromotive force and F is one faraday.[2] On account of the fact, however, that nickel chloride takes on water of crystallization, a slight modification of the ideal process by which the nickel and chlorine are allowed to unite reversibly is necessary.

Nickel chloride, in contact with water, forms the hydrate $NiCl_2.6H_2O$.[3] A hydrate with four molecules has also been detected,[4] but this existed in contact with a saturated solution at a temperature about 80° and, consequently, would not enter into this process. According to Lescoeur, the anhydrous salt is produced directly on dehydrating that with two molecules of water. This conclusion is based on vapor pressure measurements at 100°, starting with $NiCl_2.2H_2O$ and making measurements after successive evacuations of the apparatus. The final analysis of the hydrate gave $NiCl_2.1.45H_2O$, which might be a mixture of $NiCl_2.2H_2O$—$NiCl_2.1H_2O$ or $NiCl_2.2H_2O$—$NiCl_2$. Although this point is doubtful, it will be assumed that there is no hydrate with one molecule of water.

The salt in contact with the saturated solution of nickel chloride is then $NiCl_2.6H_2O$, and in the ideal process, as nickel and chlorine unite and precipitate from the solution, water would be removed from the solution, and in order to keep the amount of water in the solution con-

[1] This Journal, 28, 731 (1906).

[2] To bring the conception of free energy increase into conformity with the present more general usage, the terms involving RT are included in ΔF. See Haber, "Thermodynamik technischer Gaserak," p. 9.

[3] Lescoeur, *Ann. chim. phys.* [6], 19, 533 (1890).

[4] Etard, *Ibid.* [7], 2, 545 (1894).

stant, this has to be supplied reversibly and isothermally at the same rate at which it is removed. This may be accomplished by means of isothermal distillation, as follows: Consider water at the temperature in question enclosed in a cylinder with a frictionless piston. Allow six moles to evaporate reversibly and isothermally. The free energy increase of the system is $-6RT$. Now separate the six mols and allow them to expand reversibly and isothermally until the pressure is equal to the vapor pressure of a saturated solution of $NiCl_2.6H_2O$. The free energy increase of the system in expansion is

$$-6RT \log \frac{p_{H_2O}}{p_{sol}},$$

if p_{H_2O} is the vapor pressure of water at T° absolute and p_{sol} is the vapor pressure of the solution. The water vapor may now be condensed reversibly into the solution, at the same rate at which it is removed by the salt crystallizing out. The free energy increase of the system in this last step is $+6RT$, so that the net result is the free energy increase, $-6RT \log \frac{p_{H_2O}}{p_{sol}}$.

$$\Delta F_1 = -2EF - 6RT \log \frac{p_{H_2O}}{p_{sol}} \qquad (1)$$

is therefore the free energy of $NiCl_2.6H_2O$, referred to gaseous chlorine at atmospheric pressure and liquid water, both at T° absolute.

The free energy of $NiCl_2.2H_2O$ may be obtained from this by allowing $NiCl_2.6H_2O$ to change reversibly into $NiCl_2.2H_2O$ and four molecules of liquid water. To do this allow four mols of water to evaporate at the vapor pressure p_1 of the system $NiCl_2.6H_2O$—$NiCl_2.2H_2O$, whereby ΔF is $-4RT$. The water vapor must now be compressed to the vapor pressure p_{H_2O} of water, in which process ΔF is

$$+4RT \log \frac{p_{H_2O}}{p_1}.$$

The water vapor is then condensed to liquid water, in which ΔF is $+4RT$.

The free energy increase then of $NiCl_2.2H_2O$ is

$$\Delta F_2 = -2EF - 6RT \log \frac{p_{H_2O}}{p_{sol}} + 4RT \log \frac{p_{H_2O}}{p_1}. \qquad (2)$$

By an exactly similar process the free energy increase caused by $NiCl_2.2H_2O$ going over to $NiCl_2$ and $2H_2O$ is

$$+2RT \log \frac{p_{H_2O}}{p_2},$$

where p_2 is the vapor pressure of the system $NiCl_2.2H_2O$—$NiCl_2$, and hence the free energy increase of formation of $NiCl_2$ is

$$\Delta F = -2EF - 6RT \log \frac{p_{H_2O}}{p_{sol}} + 4RT \log \frac{p_{H_2O}}{p_1} + 2RT \log \frac{p_{H_2O}}{p_2} = -2EF + RT \log \frac{(p_{sol})^6}{p_1^4 \cdot p^2}. \qquad (3)$$

To all the above expressions a small correction must be made for the gaseous chlorine, whose pressure will in general not be 76 cm. of mercury. Assuming the vapor pressure of the solution to be unaffected by the presence of the chlorine in the enclosed space above the chlorine couple[1] would be $b - p_{sol}$ where b = barometric pressure. The increase in free energy of the system when the chlorine expands from 76 cm. to $b - p_{sol}$ is

$$\Delta F = -RT \log \frac{760}{b - p_{sol}},$$

which must be added to the right-hand side of equation (3).

2. Potential Measurements.

The apparatus in which the potential measurements were carried out consisted of an H tube 15 cm. high with a glass stop-cock in the horizontal arm. The tubes of the vertical arms were 2 to 3 cm. in diameter. The stop-cock was not lubricated and the potential of the cell was usually measured with the stop-cock turned off.

The chlorine electrode was a smooth sheet of platinum with 10 per cent. iridium, 10 cm. long by 3 cm. wide. This was half way immersed in the solution, and chlorine gas, generated by the electrolysis of strong hydrochloric acid, bubbled over it from below. The chlorine was led from the cell by a rubber tube to a bottle containing potassium hydroxide, where it was absorbed. The pressure of the gas over the chlorine electrode was determined by a small manometer in the escape tube and by the barometer reading. The nickel electrode was formed by electrolytic deposition of nickel on platinum or copper. It is known that nickel exists both in the active and passive states and that active nickel rapidly changes over to the passive state if exposed to the oxygen of the air. Pure nickel immersed in molal nickel sulphate gives about —0.2 volt[2] while according to Muthmann and Frauenberger[3] active nickel has a potential of +0.32 volt. The nickel having this potential was prepared by electrolytic deposition on platinum "according to the directions for electro-analysis." This statement, and that which follows later, according to which the solution used was neutral nickel sulphate and the impressed voltage eight volts, are all the directions given for obtaining a nickel deposit giving the voltage quoted above. The first measurements of the nickel couple were attempts to reproduce this potential in a molal solution of neutral nickel sulphate. The measurements were made by the Poggendorf method with a Weston standard cell and Lippmann electrometer. The potential between the nickel sulphate and

[1] See THIS JOURNAL, 28, 733.

[2] All single potentials in this paper refer to the "normal electrode" as —0.560 volt at 20°.

[3] *Sitzungsber. kgl. Bayr. Akad. Wiss.*, 34, 201 (1904).

normal potassium chloride was eliminated by a saturated solution of potassium chloride or ammonium nitrate placed between the two.[1] The potential was measured within thirty seconds after plating. It was found that on electrolyzing a neutral sulphate solution at room temperature with eight volts a green deposit appeared on the cathode whose potential was about that given by Muthmann and Frauenberger, and which decreased rapidly. On heating a solution containing 60 grams $NiCl_2.6H_2O$ per liter to 90° and electrolyzing with 12.5 volts the nickel came down in a black spongy form, and no green compound was visible. The highest potential obtained was +0.112 volt. Many other solutions were used, but none gave such high results as the neutral sulphate. For example, a solution containing 60 grams $NiSO_4.6H_2O$ + 20 grams $(NH_4)_2SO_4$ + 40 cc. NH_4OH per liter, electrolyzed at 20° with eight volts, gave a deposit of nickel whose potential was +0.017 volt. This was a gray, firm deposit, and could be easily duplicated. Our only explanation of Muthmann and Frauenberger's high value for nickel is that some of this green precipitate came down with the nickel. If this nickel was obtained in a cold solution with eight volts, this is certain to have happened. The nickel deposits obtained in the hot solution did not maintain a constant voltage, but fell off as rapidly as in the case of the green precipitate obtained in the cold. Attempts to increase the voltage by polarizing with hydrogen were not successful. In preparing the nickel electrodes for the final measurements the anode and cathode were separated by the wall of a porcelain cup and in all cases pure electrolytic nickel anodes were used. This cup was to protect the cathode from any sulphuric acid set free at the anode, as it was found, as stated by Muthmann and Frauenberger, that any free acid reduced the potential.

The actual measurement of the cell

$$\text{Nickel} \mid \text{Sat. sol. } NiCl_2.6H_2O \mid Pt + Cl_2$$

at 20° was now taken up. A saturated solution of the chloride was prepared by rotating bottles for several days in a thermostat maintained at 20° by means of a mercury regulator and electric lamps. The dissolved nickel was determined by electro-analysis and three determinations gave 60.5, 60.6 and 60.9 grams of anhydrous salt per hundred grams of water. This is somewhat less than 64 g. chloride to 100 g. water as found by Etard.[2] The density of this solution referred to water at 4° was 1.474.

Before making measurements, chlorine was allowed to bubble over the platinum-iridium plate for an hour or so, so as to give the solution in this arm of the H tube time to get saturated with chlorine and to drive out all air above the solution. After leaving the cell it was tested by

[1] Bjerrum: *Z. physik. Chem.*, **53**, 428 (1905).

[2] Landolt-Börnstein-Meyerhoffer Tables, 3rd Edition, p. 562.

absorbing in potassium iodide in an inverted test tube. The absence of bubbles showed the gas to be pure chlorine. The electromotive force of this couple was measured against the "normal electrode" and was found to be —1.59 volt. The nickel electrode was now prepared as described above and changed from the plating solution to the cell as quickly as possible and the reading on the bridge taken immediately. This could be done within thirty seconds from the time the plating was finished. Cleaning off the sulphate adhering to the elctrode by dipping in water did not affect the result. The electromotive force of the cell thus measured varied between 1.65 and 1.707 volts, the latter being the highest value obtained in a large number of measurements. This, therefore, corresponds to the most active nickel obtained above. The pressure of the chlorine gas at the time of the latter measurement was 752 mm. mercury.

As there is approximately 0.2 volt difference between the highest value here obtained and that which would have resulted if the nickel couples had as high a value as that assigned them by Muthmann and Freuenberger, some decomposition point determinations of the saturated solution between small platinum plates were made for the purpose of determining whether the above measured value is reversible. The values obtained were not used for computing the free energy, but were simply to decide whether an error of 0.2 volt in the above value were possible. The values found were 1.61, 1.63, 1.60 and 1.60 volts. These are somewhat less than the highest value found above, but the agreement indicates that 1.7 volts and not 1.9 volts is the voltage of the cell.

3. Vapor Pressures.

The vapor pressure of the saturated solution of nickel chloride has been found by Lescoeur[1] to be 8.0 mm. Hg and that of the system $NiCl_2.6H_2O$—$NiCl_2.2H_2O$ to be 4.6 mg, Hg, both at 20°. The system $NiCl_2.2H_2O$—$NiCl_2$ was found to have a vapor pressure at 100° of 123 mm. No measurement is given of this quantity at 20°, but the statement is made that it is zero, which is, of course, impossible.

By means of the integrated van't Hoff formula this pressure could be calculated, however, from the pressure at 100°, if the heat of hydration of $NiCl_2.2H_2O$ were accurately known. This is equal to the difference between the heat of hydration of $NiCl_2.6H_2O$ starting from $NiCl_2$ and from $NiCl_2.2H_2O$. The former quantity is 20,330 calories.[2] The following table shows the latter value, q, obtained from Lescoeur's vapor pressure of the system $NiCl_2.6H_2O$—$NiCl.2H_2O$ by the formula:

$$4.57 \log_{10} \frac{p_2}{p_1} = q_1 \left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

[1] *Ann. chim. phys.* [6], 19, 533 (1890).

[2] Landolt-Börnstein-Meyerhoffer Tabellen, p. 461.

All except the last column are taken from Lescoeur.

Temp.	Pres. in mm. Hg.	q_1.
15°	3.4	10540
25°	6.3	
20°	4.6	14760
30°	10.5	
40°	24.0	14000
15°	3.4	
30°	10.5	15470
40°	24.0	

Subtracting the average value of q_1 from 20,330, the heat of hydration of $NiCl_2.2H_2O$ is obtained. Computing this from the value of the vapor pressure of $NiCl_2.2H_2O$ at 20°, 11.5 mm. results, which is greater than that of $NiCl_2.6H_2O$, and is therefore impossible. It is evident, therefore, that this value of the heat of hydration is not accurate enough for this purpose.

The value of this pressure was obtained directly by the tensimeter method. For this purpose one tensimeter was filled in June and three in July.[1] One bulb contained phosphorus pentoxide and the other the salt. The liquid in the manometer was cottonseed oil of specific gravity 0.9185. The tensimeters were placed on their side, carefully pumped out, and at the same time warmed. They were then left several hours in connection with the pump and again pumped out and warmed before sealing off. In October they were placed in a thermostat at 20° and allowed to remain until January. The following table gives the readings in mm. of oil:

Date.	No. 1.	No. 2.	No. 3.	No. 4.
Dec. 30	11.4	7.0	3.6	5.4
Jan. 7	....	6.3	broken	6.4
Jan. 25	11.6	6.8	....	6.1
Mol water to 1 mol salt	2.06	2.05	....	1.99

Dec. 30, after the measurements, the bulbs of Nos. 2 and 5 containing the $NiCl_2$ were placed in a beaker of hot water for a few minutes to see if the evolution of water vapor could not be accelerated. The pressure increased to 10 to 15 cm. of oil, due evidently to the expansion of water vapor already present, but went back to nearly the same values afterwards. The water in the salt in the tensimeters was determined by analyzing for the amount of nickel present subsequent to these measurements, and the results were those shown in the table above. It is evident from the above that No. 1 was not properly filled, and is therefore omitted in taking the mean. The average of Nos. 2 and 4 is 0.43 mm. of mercury.

In order to check this value by a different method it was decided to

[1] See Findlay, "The Phase Rule", p. 88.

measure it at 110° and compute by the van't Hoff equation from this and from Lescoeur's value at 100°, the value at 20°.

For this purpose a tensimeter was filled with some nickel chloride that had been in the drying closet for more than a week at 100°. Mercury was used in the manometer and phosphorus pentoxide in the drying bulb. It was first placed in a steam-bath to see that it checked with Lescoeur's value. The tensimeter was left at four in the afternoon, and next morning was found at 123 mm. Hg, reduced to zero degrees, at which pressure it remained constant for the following twenty-four hours. This agrees identically with Lescoeur's value. It was then placed in a bath of vapor from boiling toluene and in a few hours reached a constant pressure of 218 mm. Hg., at a temperature of 110.7° as obtained from a thermometer corrected at this point by a standard from the Reichsanstalt. The value at 20° computed from this is 0.46 mm.

The tensimeter was then opened and heated while exhausted and connected to the air pump for an hour and a half at a temperature varying from between 90° and 120°, thereby driving off some water. It was sealed off while hot and again placed in the bath of toluene vapor. The constant pressure reached as before in a few hours was 216 mm. Hg., at 110.6°. The pressure computed from this measurement for 20° is 0.47 mm.

These values agree well enough for the present purpose with the average of those from direct measurements. The best value to adopt is the average of the four which is 0.45 of mercury. It is interesting to note that on cooling, the mercury in the tensimeter immediately goes back to nearly a zero pressure, showing that water is taken up by the chloride more rapidly than it is evolved.

Substituting in formula (3) $E = 1.71$ volts, $p_{sol} = 8.0$, $p_1 = 4.6$ and $p_2 = 0.45$, $\Delta F = -74{,}400$ cal. The correction due to the pressure of the chlorine not being 760 mm. is negligible.

The heat of the reaction, or the increase in total energy, is —74,500 cal., assuming the compound to be formed from gaseous chlorine. If the chlorine were solid and superheated to this temperature, the total energy increase is obtained by increasing the above value by the sum of the heat of fusion and the heat of vaporization of chlorine which has been estimated at 7000 cal.[1] This gives —67,500 cal. as the total energy change, starting with solid chlorine. Likewise, if the chlorine were solid the free energy increase ΔF would be diminished by the quantity RT, or approximately 600 cal., giving the value F = —75,000. The ratio of free to total energy, for chlorine in the solid state, consequently is 1.11, while the ratio of the same quantities with chlorine in the gaseous state is 1.00. The free energy and the total energy of this salt, therefore, are

[1] This Journal, 28, 741 (1906).

approximately equal, as was found to be true in all other cases for which this calculation has been made.

4. Precision Discussion.

The term $2EF$ in formula (3) amounts to 79,040 calories, the second term to only 4600 cal., from which it is evident that even a large error in the vapor pressures would have only a relatively small effect on the final result. Assuming an error of 0.1 mm. in p_{sol}, p_2 and 0.1 mm. in p, which seems an outside limit, the resultant effect is 600 calories, or about 0.8 per cent. error in ΔF. Assuming a possible error of 0.02 volt in E the combined error in ΔF would be 990 cal., or 1.3 per cent.

5. Summary.

The free energy ΔF of $NiCl_2$ was determined by measuring the potential of the cell.

$$Ni \mid \text{Sat. sol. of } NiCl_2.6H_2O \mid Cl_2 + Pt.$$

A formula for ΔF was deduced, involving this potential, the vapor pressure of the saturated solution, of the system $NiCl_2.6H_2O$—$NiCl_2.2H_2O$ and of $NiCl_2.2H_2O$—$NiCl_2$. The pressure of the last system was obtained both by direct and by indirect measurement. The free energy and total energy of $NiCl_2$ were found to be approximately equal.

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A STUDY OF THE SOLUTIONS OF SOME SALTS EXHIBITING NEGATIVE VISCOSITY.

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In 1873 Hübner[1] determined the viscosities of a series of solutions of alkaline halides of equal densities and observed that some of the salts diminished the viscosity of water.

Subsequently Sprung[2] made an extensive study of the viscosities of saline solutions between the temperatures 0° and 60° C.

He divided the salts examined into two groups as follows:

(1) KCl, KBr, KI, KNO_3, $KClO_3$, NH_4Cl, NH_4Br, NH_4NO_3.

(2) K_2SO_4, NaCl, NaBr, NaI, $NaNO_3$, $NaClO_3$, Na_2SO_4, $(NH_4)_2SO_4$, $BaCl_2$, $SrCl_2$, $CaCl_2$, LiCl, $MgSO_4$.

He pointed out that at low temperatures the salts of the first group lower the viscosity of water and at higher temperatures they increase it. The salts of the second group always increase the viscosity of the solvent, the viscosity of the solution becoming less as the temperature is raised.

[1] *Pogg. Ann.*, 157, 130.
[2] *Ibid.*, 159, 1.

The experimental work of Sprung was later confirmed by the investigations of Slotte[1] and Wagner,[2] the latter having studied the viscosities of the solutions of forty different salts at several concentrations.

Arrhenius,[3] Kanitz[4] and Mützel[5] have measured the viscosities of saline solutions which show the phenomenon of negative viscosity and still more recently Ranken and Taylor[6] have made some extremely accurate determinations of the viscosities of solutions of potassium chloride and ammonium iodide at different temperatures.

One of the first to offer an explanation of negative viscosity was Euler,[7] who made use of the theory of electrostriction proposed by Nernst and Drude.[8] In terms of this theory the ions are enveloped in a strong electric field, owing to their charges, and the intervening liquid is subjected to great stress, so that the tendency of the ions to increase the viscosity in inverse proportion to their speeds of migration is offset by the electrostriction.

Wagner[9] has pointed out that Euler's theory is untenable, since the viscosity of the solvent may be diminished by solutes which are non-electrolytes.

As a possible explanation of the phenomenon, Wagner suggests that the amount of solvent in a given space is diminished by the solute and that this leads to a lowering of the viscosity.

If the solute have a high viscosity, then the viscosity of the solution will be greater than that of the solvent.

Ranken and Taylor[10] have pointed out that at 8° urea diminishes the viscosity of water, but as the temperature is raised the viscosity of the solution becomes greater than that of the solvent.

Recently the author[11] determined the viscosities of several solutions of potassium salts having lower viscosities than that of the slovent. The determinations were extended from dilute to concentrated solutions and it was found that in every case the viscosity-concentration curves passed through a minimum.

The suggestion was put forward that the abnormal behavior of the potassium salts resulted from the combined action of the ions and the undis-

[1] *Wied. Ann.*, **20**, 257.
[2] *Z. physik. Chem.*, **5**, 31.
[3] *Ibid.*, **1**, 285.
[4] *Ibid.*, **22**, 336.
[5] *Wied. Ann.*, **43**, 15.
[6] *Trans. Roy. Soc., Edinburgh*, **45**, 397.
[7] *Z. physik. Chem.*, **25**, 536.
[8] *Ibid.*, **15**, 79.
[9] *Ibid.*, **46**, 867.
[10] *Loc. cit.*
[11] *J. chim. phys.*, **5**, 344.

sociated molecule. The potassium ion appearing to lower the viscosity of the solvent, while the different anions and the undissociated molecules tended to increase it.

Shortly after this paper was written Jones and Veazey[1] suggested a possible explanation of negative viscosity.

In the course of their investigations the anomalous behavior of potassium thiocyanate directed their attention to this phenomenon and they found that the solutes which diminish the viscosity of water are those whose cathions have large atomic volumes. If the ions of the solute are large, relative to the molecules of the solvent, then the effect of the dissolved salt will be to reduce the viscosity of the solvent.

In view of what has been done in this field it has seemed of sufficient importance to extend my work and include other saline, aqueous solutions exhibiting negative viscosity.

The salts chosen for more careful study were ammonium chloride, ammonium bromide, ammonium iodide, ammonium nitrate, and rubidium iodide.

Apparatus and Method.

The method of measuring the viscosities was the well-known transpiration method of Poiseuille-Ostwald. The viscometers were placed in a bath of water maintained at constant temperature and the times of transpiration were measured with a stop-watch which had been carefully compared with an accurate chronometer.

The densities were determined with a pycnometer of the Sprengel-Ostwald type.

The viscometers were frequently cleaned with chromic acid and special precautions were taken to protect them from dust.

The constants of the tubes were frequently checked by measuring the times of transpiration of pure distilled water and solving for k in the formula

$$k = \frac{\eta}{dt},$$

where η is the absolute viscosity of water at a definite temperature, d the density of water at the same temperature, and t the time of transpiration as measured by the stop-watch.

The values of η and d were obtained from the tables of Landolt and Börnstein.

The concentration of the solutions was determined either by direct weighing or by analysis.

The salts used were obtained from Kahlbaum and were sufficiently pure to warrant using them without recrystallization.

[1] *Am. Chem. J.*, 37, 405.

Results.

In the tabulation of results the symbols have the following significance:

m = concentration of solution in gram-molecules per liter.
d = density of solution referred to water at 4° C.
η = viscosity in C. G. S. units (dynes per square centimeter).

TABLE I.

NH_4Cl—25°.

m.	d.	η.
0.4437	1.0071	0.00889
0.8874	1.0138	0.00885
1.3311	1.0204	0.00882
1.7748	1.0268	0.00880
2.2185	1.0331	0.00878
2.6622	1.0394	0.00887
3.1059	1.0458	0.00897
3.5496	1.0516	0.00904
4.437	1.0630	0.00925

TABLE II.[1]

NH_4Cl.

m.	$\eta_{10°}$.	$\eta_{30°}$.	$\eta_{50°}$.
0.68	0.0128	0.0080	0.0057
1.62	0.0123	0.0081	0.0058
2.93	0.0120	0.0082	0.0061
4.34	0.0120	0.0085	0.0064

TABLE III.

NH_4Br—25°.

m.	d.	η.
0.216	1.0121	0.008867
0.432	1.0247	0.008796
0.647	1.0352	0.008756
0.863	1.0468	0.008680
1.079	1.0583	0.008644
1.323	1.0715	0.008575
1.588	1.0858	0.008480
2.646	1.1414	0.008254
3.486	1.1758	0.008356
4.357	1.2273	0.008470
4.920	1.2605	0.008560

TABLE IV.[2]

NH_4Br.

m.	$\eta_{10°}$.	$\eta_{30°}$.	$\eta_{50°}$.
1.63	0.0116	0.0077	0.0056
2.58	0.0112	0.0077	0.0057
3.76	0.0111	0.0079	0.0061

[1] Sprung, *Pogg. Ann.*, **159**, 1.
[2] Sprung, *Loc. cit.*

TABLE V.

NH_4I---25°.

m.	*d.*	*η.*
0.500	1.0447	0.008577
0.751	1.0675	0.008440
1.001	1.0913	0.008237
1.501	1.1377	0.008086
2.002	1.1839	0.007827
2.502	1.2304	0.007779
3.002	1.2765	0.007842
4.003	1.3692	0.007997
5.004	1.4591	0.008321

TABLE VI.

NH_4I—30°.

m.	*d.*	*η.*
0.125	1.0071	0.00792
0.25	1.0181	0.00786
0.5	1.0401	0.00774
1.0	1.0944	0.00753
4.0	1.3513	0.00729
6.0	1.5285	0.00823

TABLE VII.[1]

NH_4I—45°.

m.	*d.*	*η.*
0.125	1.0026	0.005950
0.25	1.0145	0.005925
0.5	1.0380	0.005855
1.0	1.0853	0.005780

TABLE VIII.

NH_4I.

t.	*m.*	*d.*	*η.*
10	1.001	1.0944	0.01146
15		1.0937	0.01031
20		1.0929	0.009277
10	2.002	1.1889	0.01044
15		1.1874	0.009568
20		1.1859	0.008752
10	3.002	1.2826	0.009947
15		1.2806	0.009297
20		1.2786	0.008648
10	4.003	1.3763	0.00001
15		1.3738	0.00931
20		1.3717	0.008692
10	5.004	1.4661	1.01051
15		1.4641	0.009761
20		1.4611	0.009017

[1] Ranken and Taylor, *Loc. cit.*

TABLE IX.

NH_4NO_3—25°.

m.	*d.*	*η.*
0.256	1.0059	0.008853
0.512	1.0137	0.008797
0.767	1.0215	0.008724
1.023	1.0300	0.008655
1.279	1.0373	0.008602
1.454	1.0432	0.008579
2.012	1.0602	0.008504
2.245	1.0676	0.008500
2.587	1.0777	0.008565
2.909	1.0873	0.008627
3.636	1.1078	0.008850
4.664	1.1396	0.009308

TABLE X.[1]

NH_4NO_3.

m.	$\eta_{10°}$.	$\eta_{30°}$.	$\eta_{50°}$.
0.745	0.0124	0.0079	0.00567
1.521	0.0119	0.0079	0.0057
3.367	0.0120	0.0085	0.0062
4.646	0.0128	0.0091	0.0070
6.22	0.0145	0.0113	0.0088

TABLE XI.

RbI—25°.

m.	*d.*	*η.*
0.264	1.0371	0.008714
0.528	1.0592	0.008489
0.792	1.1225	0.008303
1.056	1.1738	0.008147
1.583	1.2475	0.007887
1.758	1.2662	0.007918
2.639	1.4149	0.007796
2.931	1.4612	0.007870

In Fig. 1 the tabulated values of viscosity $\times 10^4$ are plotted as ordinates against the corresponding concentrations as abscissae. For convenience in comparison, Fig. 2 gives similar data for the corresponding potassium salts and for sodium chloride and sodium bromide. The curves in Fig. 1 are for 25° while those in Fig. 2 are for 18°.

The viscosity-concentration curves preserve the same order for the three bases, sodium, potassium and ammonium and apparently rubidium. In all cases the chlorides have the greatest and the iodides the least viscosity.

The ammonium salts depress the viscosity of water to a greater extent than the corresponding potassium salts, while rubidium iodide produces the maximum effect of all.

[1] Sprung, *Loc. cit.*

m.
Fig. 1.

In terms of the theory put forward by the author the minima in the viscosity-concentration curves are explained as due to equilibrium between the tendency of the cathions to diminish the viscosity of the solvent and the tendency of the anions and the undissociated molecules to increase it.

At the minimum we find the solutions to be approximately 70 per cent. ionized.

Viscosity and Temperature.

Early in the study of the viscosity of pure liquids and solutions it was discovered that a slight variation in temperature produced a decided change in the viscosity, generally the viscosity being diminished by rise of temperature.

The attempts which have been made to express viscosity as a function of the temperature have been but partially successful.

Slotte[1] found that the viscosities of a series of chromate solutions at temperatures between 10° and 40° could be quite accurately determined by means of the formula

$$\eta = \frac{\gamma}{\alpha + t} - \beta, \qquad (1)$$

[1] *Wied. Ann.*, 14, 21.

where α, β, and γ are constants and t is the temperature.

Subsequently the same investigator[1] proposed the formula

$$\eta = \frac{c}{(\alpha + t)^n}, \tag{2}$$

α and c being constants and the exponent n varying in value from 1.6 to 1.9.

m.

Fig. 2.

From purely theoretical reasoning Graetz[2] suggested the formula

$$\eta = A\,\frac{t_c - t}{t - t_f},$$

in which A is a constant, t_c and t_f the critical and melting temperatures, respectively, and t the temperature at which the viscosity of the liquid is sought. This formula has been found to give good results for pure liquids within a limited range of temperature.

De Heen[3] has proposed the formula

$$\eta = \left[\frac{e^{\frac{t}{n}} + A\eta_0^{\frac{t}{t}} - 1}{Ae^{\frac{t}{n}}}\right],$$

[1] *Beibl.*, 16, 182.

[2] *Wied. Ann*, 24, 25.

[3] *Bull. Ac. Belg.* (3), 11, 29.

where η_0 is the viscosity at 0° and A and n are constants.

Of the several formulae enumerated those of Slotte and Graetz appear to be most widely applicable.

The effect of change in temperature on the viscosities of the solutions studied is shown in Figs. 3 to 6, in which are given a series of viscosity-concentration isothermals.

Fig. 3.

The solutions of ammonium chloride, ammonium bromide and ammonium nitrate become less and less negatively viscous as the temperature is raised, until at 50°, the temperature of the highest isothermals, they are all positive.

Ammonium iodide exhibits the same tendency but because of its marked negative viscosity it is evident that a higher temperature must be reached before the viscosity changes sign. The minimum in the viscosity-concentration isothermals shifts toward the more dilute region as the temperature is raised.

Since the isothermals are not parallel, it is evident that the rate of change of viscosity is not uniform at different temperatures.

The viscosities of thermal solutions of the salts studied in this and a

m.
Fig. 4.

previous investigation[1] can be calculated with a fair degree of accuracy by formula (1) of Slotte.[1]

Tables XII to XXII give the observed and calculated values of η for different temperatures together with their differences, Δ. In every case the greatest difference occurs in the values for 10°, the calculated value being, with but two exceptions, too large. It is evident that the formula ceases to be applicable below 15°.

Neglecting the values for 10° and eliminating several values which are known to be slightly in error, the average departure from the observed value is 8 units in the fifth place of decimals.

The results for three salts, ammonium chloride, ammonium iodide and potassium chloride, are shown graphically in Fig. 7, the observed values being designated by a cross and the calculated by a small circle.

TABLE XII.

NaCl.

$\alpha = 27.$ $\beta = 0.0007.$ $\gamma = 0.5523.$

t.	η(Observed).	η(Calculated).	Δ.
17.6	0.01163	0.01168	—0.00005
18	0.0116	0.01157	+0.00003
20	0.01109	0.01105	+0.00004
25	0.00978	0.00992	—0.00014

[1] *Loc. cit.*

TABLE XIII.

NaBr.

$\alpha = 27.$ $\beta = 0.0011.$ $\gamma = 0.5523.$

$t.$	η(Observed).	η(Calculated).	$\Delta.$
10	0.01358	0.01383	—0.00025
25	0.00948	0.00952	—0.00004
30	0.00853	0.00859	—0.00006
50	0.00610	0.00607	—0.00003

TABLE XIV.

$NaNO_3$.

$\alpha = 27.$ $\beta = 0.00103$ $\gamma = 0.5523.$

$t.$	η(Observed).	η(Calculated).	$\Delta.$
10	0.0138	0.0139	—0.00010
17.6	0.01118	0.01135	—0.00017
20	0.01107	0.01066	+0.00041
25	0.00949	0.00959	—0.00010
30	0.00866	0.00866	0.00000
50	0.00617	0.00614	+0.00003

TABLE XV.

KCl.

$\alpha = 30.$ $\beta = 0.00101.$ $\gamma = 0.05520.$

$t.$	η(Observed).	η(Calculated).	$\Delta.$
10	0.01270	0.01279	—0.00009
18	0.01055	0.01049	+0.00006
20	0.01004	0.01004	0.00000
25	0.00902	0.00902	0.00000
30	0.00814	0.00819	—0.00005
50	0.00580	0.00589	—0.00009

TABLE XVI.

KBr.

$\alpha = 30.$ $\beta = 0.00124.$ $\gamma = 0.5520.$

$t.$	η(Observed).	η(Calculated).	$\Delta.$
10	0.01222	0.01256	—0.00033
18	0.01030	0.01026	+0.00004
30	0.00796	0.00796	0.00000
50	0.00574	0.00566	+0.00008

TABLE XVII.

KI.

$\alpha = 30.$ $\beta = 0.0015.$ $\gamma = 0.5520.$

$t.$	η(Observed).	η(Calculated).	$\Delta.$
10	0.01180	0.01230	—0.00050
18	0.01007	0.01000	+0.00007
30	0.00760	0.00770	—0.00010
50	0.00553	0.00540	+0.00013

TABLE XVIII.

KNO_3.

$\alpha = 30.$ $\beta = 0.0010.$ $\gamma = 0.5520.$

t.	η(Observed).	η(Calculated).	Δ.
10	0.01242	0.01280	+0.00038
18	0.01044	0.01050	—0.00006
20	0.00995	0.01004	—0.00009
30	0.00820	0.00820	0.00000
40	0.00690	0.00689	+0.00001
50	0.00585	0.00590	—0.00005

TABLE XIX.

NH_4Cl.

$\alpha = 30.$ $\beta = 0.0011.$ $\gamma = 0.5520.$

t.	η(Observed).	η(Calculated).	Δ.
10	0.01275	0.01270	+0.00005
17.6	0.01040	0.01049	—0.00009
25	0.00808	0.00893	—0.00005
30	0.00808	0.00810	—0.00002
50	0.00578	0.00580	—0.00002

TABLE XX.

NH_4Br.

$\alpha = 30.$ $\beta = 0.0015.$ $\gamma = 0.5520.$

t.	η(Observed).	η(Calculated).	Δ.
10	0.01220	0.01230	—0.00010
25	0.00866	0.00953	—0.00087
30	0.00780	0.00770	+0.00010
50	0.00570	0.00540	+0.00030

TABLE XXI.

NH_4I.

$\alpha = 30.$ $\beta = 0.0018.$ $\gamma = 0.5520.$

t.	η(Observed).	η(Calculated).	Δ.
10	0.01146	0.01200	—0.00054
15	0.01031	0.01047	—0.00016
20	0.00928	0.00924	+0.00004
25	0.00824	0.00823	+0.00001
30	0.00753	0.00740	+0.00013
50	0.00578	0.00556	+0.00022

TABLE XXII.

NH_4NO_3.

$\alpha = 30.$ $\beta = 0.0013.$ $\gamma = 0.5520.$

t.	η(Observed).	η(Calculated).	Δ.
10	0.01223	0.01250	—0.00027
25	0.00866	0.00873	—0.00007
30	0.00790	0.00790	0.00000
50	0.00568	0.00560	+0.00008

Viscosity and Conductivity.

As early as 1856, G. Wiedemann[1] called attention to the fact that viscosity and conductivity are related. From a study of solutions of copper sulphate he was led to formulate the relation

$$\frac{k\eta}{m} = \text{constant},$$

where η is the viscosity and k is the conductivity of the solution whose concentration is m.

Gotrian[2] measured the viscosity and conductivity of solutions at different temperatures, but failed to establish any clear relation between them.

m.

Fig. 5.

Later, Grossman[3] recalculated Gotrian's results and found that the product of the viscosity by the conductivity was a constant, independent of the temperature.

Several empirical relations have been pointed out by various workers,

[1] *Pogg. Ann.*, 99, 229.
[2] *Ibid.*, 157, 130.
[3] *Wied. Ann.*, 18, 119.

among whom may be mentioned Arrhenius,[1] Euler,[2] Strindberg,[3] and Holland.[4]

In 1896 Moore,[5] in an investigation of the viscosities of some salt solutions, attempted to find some relation between viscosity and conductivity, but without much success. He makes the significant remark

m.

Fig. 6.

that "more extended observations must be made upon the relation of viscosity and conductivity, perhaps even some new method of comparison arrived at, before the two subjects are placed in their right relation."

The recent work of Bousfield and Lowry[6] has led to the formula

$$\frac{k_t}{k_0}=\frac{\rho_v}{\rho_0}(1+bt)^n e^{-at}$$

connecting conductivity and temperature, the parenthesis being Slotte's expression for the change in viscosity with temperature.

[1] *Z. physik. Chem.*, 9, 487.
[2] *Ibid.*, 35, 536.
[3] *Ibid.*, 14, 221.
[4] *Wied. Ann.*, 50, 261.
[5] *Phys. Rev.*, 3, 321.
[6] *Proc. Roy. Soc.*, 74, 280.

It seemed of interest to compare the viscosities of the normal solutions with their conductivities as given by Kohlrausch,[1] making use of Wiedemann's relation.

t.

Fig. 7.

The results are given in Table XXIII, λ denoting the equivalent conductivity.

TABLE XXIII.

Temp. = 18°.

	η.	λ	$\eta\lambda$.
NaCl	0.0116	74.4	0.863
NaBr	0.0115	70.5	0.811
$NaNO_3$	0.0114	66.0	0.752
KCl	0.0105	98.2	1.031
KBr	0.0103	103.7	1.069
KI	0.0101	103.4	1.041
KNO_3	0.0104	80.4	0.839
NH_4Cl	0.0103	97.0	0.999
NH_4Br	0.0101	102.9	1.039
NH_4I	0.00977	104.0	1.016
NH_4NO_3	0.0101	88.9	0.901

[1] *Das Leitvermögen der Elektrolyte.*

The values of $\eta\lambda$ for the halogen salts of potassium and ammonium are nearly constant, the average value being 1.032.

It is evident, however, that some other factor besides those given is required to establish the relation between viscosity and conductivity.

Discussion of Results.

A survey of the results obtained with the potassium, ammonium and rubidium salts examined seems to confirm the theory suggested by the author, that the phenomenon of negative viscosity is due to a tendency of the cathions to lower the viscosity of the solvent while the anions and the undissociated molecule tend to increase it. Jones and Veazey[1] have called attention to the fact that those salts whose cathions have the greatest atomic volumes exhibit negative viscosity when dissolved, provided the atomic volumes of the anions are not so small as to counteract the effect of the cathions.

In terms of their theory we should expect, for a series of salts having the same anion, that the lowering of the viscosity would vary directly with the atomic volume of the cathion. These authors have shown this to be approximately true for the normal solutions of the chlorides of potassium, rubidium and caesium. From Figs. 1 and 2 we find that rubidium iodide lowers the viscosity to a greater extent than potassium iodide while the lowering produced by ammonium iodide is slightly less than that produced by rubidium iodide. Owing to scarcity of material it was impossible to extend the measurements on rubidium iodide to more concentrated solutions.

Differences in the degree of dissociation at different temperatures cannot be employed to explain the greater negative viscosity observed in each case for the lower temperaures.

It is probable that the lower temperatures favor the formation of molecular complexes which, owing to greater volume and smaller surface, tend to diminish the viscosity.

Dunstan[2] has furnished experimental evidence for the formation of these complexes, which are stable only at relatively low temperatures.

By means of this supposition it is possible to explain the case of negative viscosity presented by urea at 8° and other instances of negative viscosity observed with solutions of non-electrolytes.

The empirical formula of Slotte for calculating viscosities at various temperatures is found to apply to the solutions studied between 15° and 20°.

Assuming with Wiedemann that the migration velocity varies inversely with the viscosity for a fixed potential gradient, the product of

[1] Jones and Veazey, *Loc. cit.*

[2] *J. Chem. Soc.*, **85**, 817; *Z. physik. Chem.*, **49**, 590.

the viscosity and conductivity should give a constant. It has been found that this relation is only approximately true for the solutions investigated.

COLUMBIA UNIVERSITY, March, 1908.

THE ACTION OF VARIOUS ANHYDROUS CHLORIDES ON TELLURIUM AND ON TELLURIUM DIOXIDE.

BY VICTOR LENHER.

Received February 25, 1908.

In an earlier paper[1] the action of sulphur monochloride on elementary tellurium has been shown to result in the production of tellurium tetrachloride and sulphur, when the sulphur monochloride is in excess, while Krafft and Steiner,[2] in studying this reaction, observed that when an excess of tellurium is heated with sulphur monochloride, tellurium dichloride results.

Further study on the action of tellurium and the dioxide with active reagents has shown that with many of the anhydrous chlorides, especially with those which are liquid at the ordinary temperature, tellurium tetrachloride is produced. In certain cases the tetrachloride immediately separates from the solution in pure form while with a number of reagents of this character actual union takes place and a crystalline condensation product separates.

Tellurium Dioxide and Sulphur Monochloride.—Tellurium dioxide, when treated with an excess of sulphur monochloride, is transformed into the tetrachloride, sulphur dioxide being formed at the same time, according to the equation:

$$TeO_2 + 2S_2Cl_2 = TeCl_4 + SO_2 + 3S.$$

Analysis, $TeCl_4$: Calculated, Cl, 52.79; Te, 47.21.
Found, Cl, 52.07; Te, 46.65.

When, on the other hand, an excess of tellurium dioxide is heated with sulphur monochloride, the reducing action of this reagent steps in and the result is that the dichloride of tellurium is formed, thus:

$$TeO_2 + S_2Cl_2 = TeCl_2 + S + SO_2.$$

The formation of tellurium tetrachloride by the action of excess of sulphur monochloride on tellurium dioxide takes place readily; the reaction can be materially hastened by warming, and under these conditions, preparation of a large amount of the tetrachloride can be accomplished in a very short time. Extraction of the salt with carbon bisulphide is advisable in order to remove an excess of sulphur.

Behavior of the Oxychlorides of Sulphur toward Tellurium and Tellurium

[1] THIS JOURNAL, 24, 188.

[2] *Ber.*, 34, 560.

Dioxide.—With thionyl chloride, either the oxide of tellurium or the metal yields tetrachloride when the anhydrous chloride is in excess and dichloride when the element or oxide is in excess. These reactions are quite similar to the action of sulphur monochloride on the metal or oxide.

Sulphuryl chloride reacts with the element forming tellurium tetrachloride, but when the metal is in excess the dichloride is the resulting product. Tellurium dioxide in contact with sulphuryl chloride acts only very slowly, if at all, in the cold, but when the two are heated together in a sealed tube, crystalline products are formed which, by analysis, appear to be due to the simple solution of the dioxide in the sulphuryl chloride and subsequent recrystallization of condensation products. The end products of the reaction are dependent on the reacting masses and on the pressure at which the reaction is carried out.

Tellurium and Thionyl Chloride, with C. W. Hill.—Tellurium and thionyl chloride, when heated together in a sealed tube for twenty-four hours, yield crystals of the tetrachloride. The supernatant liquid was dark colored and was found to contain tellurium.

Analysis, $TeCl_4$:	Calculated,	Cl, 52.79;	Te, 47.21.
	Found,	Cl, 52.00;	Te, 47.47, 46.60.

In studying the action of thionyl chloride on tellurium it was found most satisfactory to heat the metal in a porcelain boat in a current of the vapor of thionyl chloride, which was produced by boiling thionyl chloride in a distilling bulb. The boat in which the tellurium was contained was placed in a combustion tube connected directly with the distillation bulb, and the combustion tube was drawn out into a series of bulbs. This apparatus was chosen inasmuch as the arrangement allowed the products of the reaction, by carefully regulating the temperature, to be carried from bulb to bulb, and in the first bulbs practically all of the sulphur formed in the reaction was retained, allowing the tellurium tetrachloride to be collected in the bulbs farthest from the boat.

Analysis, $TeCl_4$:	Calculated,	Cl, 52.79;	Te, 47.21.
	Found,	Cl, 52.80, 52.20;	Te, 47.01, 46.95.

The reaction of thionyl chloride on tellurium may be expressed,

$$2SOCl_2 + Te = TeCl_4 + SO_2 + S.$$

Thionyl Chloride and Tellurium Dioxide, with C. W. Hill.—By heating thionyl chloride with tellurium dioxide for twenty-four hours in a sealed tube, long slender crystals of tellurium tetrachloride were obtained. When the tubes in which the reaction was carried out were opened sulphur dioxide was liberated.

Analysis, $TeCl_4$:	Calculated,	Cl, 52.79;	Te, 47.21.
	Found, I,	Cl, 52.31, 52.71;	Te, 47.11, 47.64.
	" II,	Cl, 52.55, 52.13;	Te, 47.55, 47.20.

On heating the dioxide in the vapor of thionyl chloride, tellurium tetrachloride is also readily obtained. Analyses II, above.

Sulphuryl Chloride and Tellurium, with C. W. Hill.—Tellurium and sulphuryl chloride, when heated together in a sealed tube, yield tellurium tetrachloride. On heating tellurium in the vapor of sulphuryl chloride, the metal is first transformed into black dichloride, after which it is further chlorinated to the tetrachloride by the action of excess of the sulphuryl chloride.

Analysis, $TeCl_4$; Calculated, Cl, 52.79; Te, 47.21.
Found, Cl, 52.51, 52.36; Te, 47.14, 47.30.

Sulphuryl Chloride and Tellurium Dioxide, with C. W. Hill.—Tellurium dioxide acts quite differently toward sulphuryl chloride than it does with thionyl chloride or sulphur monochloride. When heated in the vapor of sulphuryl chloride to as high a temperature as it is possible to conduct an experiment in hard glass combustion tubing, there is apparently no action. No volatilization of the tetrachloride occurs, and in our experiments, when a weighed amount of tellurium dioxide was heated in the vapor of sulphuryl chloride to as high a temperature as the glass would permit, the boat and contents weighed precisely the same after this treatment as before. This would indicate that under these conditions the vapor of sulphuryl chloride is without any appreciable action on tellurium dioxide.

When, however, tellurium dioxide and sulphuryl chloride are brought together in a sealed tube and heated, the system undergoes complex changes. When the dioxide was heated in a sealed tube with sulphuryl chloride for twenty-four hours at 165°, a small amount of a crystalline substance was formed, but the larger part of the dioxide remained unchanged. The heating was continued for seventy-two hours when the dioxide completely disappeared, the liquid having assumed a dark yellow color. On allowing the tube to cool, crystals deposited which were entirely unlike tellurium tetrachloride. When the tube was opened so much sulphur dioxide had been formed that the major part of the contents were lost when the pressure was released on opening the tube. The portion saved showed a content of 40.38 per cent. of chlorine.

The experiment was repeated a number of times, the tubes being heated for forty-eight hours to 175°. In each case the tube was strongly cooled before opening and in each tube a crystalline product was obtained.

Analysis showed the crystalline substances formed to vary in composition. Their composition by the analytical data obtained may be indicated as follows:

$$3TeO_2, 4SO_2Cl_2;\ 5TeO_2, 9SO_2Cl_2;\ TeO_2, 2SO_2Cl_2;\ 2TeO_2, 5SO_2Cl_2.$$

Sulphuryl chloride appears to have no action on tellurium dioxide at the ordinary temperatures or when the dioxide is heated in the vapor

of sulphuryl chloride, but when the two are heated together to high temperatures in a sealed tube, condensation products of varying composition are obtained.

In each experiment it was found that the excess of sulphuryl chloride contained large quantities of tellurium.

General Remarks.

In studying the action of the chloride of sulphur or the oxychlorides of sulphur it is observed that not infrequently one of the products of the reaction along with tellurium chloride is sulphur dioxide. Frequently in our experiments, in sealed tubes, large volumes of sulphur dioxide escaped on opening the tubes, while in the tube itself pure white tellurium chloride remained. This is an interesting illustration of mass action, as well as of conditions in the system, since sulphur dioxide readily precipitates tellurium from an aqueous or acid solution of the chloride, and the dioxide when heated in a current of sulphur dioxide gas is readily reduced to metal.

While the action of the various chlorides of sulphur on tellurium or on tellurium dioxide goes on readily, a number of other anhydrous chlorides act similarly but not infrequently by-products are formed which contaminate the chloride of tellurium which is produced. For example, *arsenic trichloride* or *antimony trichloride* react with tellurium dioxide, yielding tellurium tetrachloride and arsenic trioxide or antimony trioxide. In these cases it is very difficult to obtain the tellurium chloride in a high degree of purity. *Lead tetrachloride* will convert either the element or the oxide to tellurium tetrachloride. Here again an impure salt is formed and a mixture is obtained from which it is difficult to obtain pure tellurium salt.

Phosphorus trichloride, in contact with the dioxide of tellurium, quickly reduces it to the elementary condition, and when brought in contact with the element in pure condition is without action.

Carbon tetrachloride is without action on tellurium or on tellurium dioxide even when allowed to be in contact with either of them for a great length of time.

Tellurium Dioxide and Antimony Pentachloride.—Antimony pentachloride reacts with tellurium dioxide in the cold, the action of heat materially hastening the reaction, with the formation of the compound $TeCl_4SbCl_5$.

Analysis, $TeCl_4.SbCl_5$: Calculated, Te, 22.49; Sb, 21.16; Cl, 56.35.
Found, Te, 22.02; Sb, 21.74; Cl, ...

The action of antimony pentachloride on tellurium dioxide can be considered as first resulting in tellurium tetrachloride, which immediately unites with an additional molecule of antimony pentachloride, forming the addition product $TeCl_4SbCl_5$:

(a) $5TeO_2 + 4SbCl_5 = 5TeCl_4 + 2Sb_2O_5$;

(b) $TeCl_4 + SbCl_5 = TeCl_4,SbCl_5$;

or $5TeO_2 + 9SbCl_5 = 5[TeCl_4,SbCl_5] + 2Sb_2O_5$.

The compound $TeCl_4.SbCl_5$ appears in white tabular crystals which are readily decomposed by water.

Phosphorus Oxychloride and Tellurium Dioxide.—When phosphorus oxychloride is brought in contact with tellurium dioxide and the two are allowed to remain together in a warm place, a crystalline mass of large flat monoclinic plates begins to form. The excess of phosphorus oxychloride can be readily removed by means of carbon bisulphide. These crystals are deliquescent and are readily decomposed by water.

Analysis, $TeCl_4.POCl_3$: Calculated, Te, 31.32; P, 7.61; Cl, 61.06.
Found, Te, 30.22; P, 7.90; Cl, 59.13.

While phosphorus oxychloride doubtless first reacts with tellurium dioxide to form tellurium tetrachloride, the tetrachloride, as soon as produced, unites with one molecule of the excess of phosphorus oxychloride forming the addition product. The first reaction could be indicated:

$$3TeO_2 + 4POCl_3 = 3TeCl_4 + 2P_2O_5,$$

and the entire reaction may be expressed:

$$3TeO_2 + 7POCl_3 = 3[TeCl_4.POCl_3] + 2P_2O_5.$$

When the above reaction is carried out with an excess of phosphorus oxychloride, a considerable portion of the reaction product remains in solution in the excess of the reagent.

It thus appears that by the action of the various anhydrous chlorides which have been studied on tellurium or tellurium dioxide, three series of products can form; either tellurium tetrachloride or the dichloride can be produced, or by the use of such compounds as phosphorus oxychloride or antimony pentachloride, double chlorides can be obtained.

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THE HOMOGENEITY OF TELLURIUM.

BY VICTOR LENHER.

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When tellurium or its dioxide reacts with a number of the liquid anhydrous chlorides,[1] crystals of tellurium tetrachloride or of a double chloride are formed along with a mother liquor which contains the excess of the reacting anhydrous chloride. This mother liquor contains such by-products of the reaction as may be soluble in it, and has also been found invariably to contain greater or less quantities of tellurium.

When sulphur monochloride is the reacting liquid, the amount of tel-

[1] See preceding paper.

lurium appearing in the excess of the reagent is quite small, so small indeed that a fairly good separation of tellurium from selenium can be effected by use of this reagent in the cold, inasmuch as selenium dissolves readily in sulphur monochloride. When, however, the sulphur chloride is warm, its solvent power on tellurium chloride is materially increased.

Other chlorides studied, such as thionyl chloride, sulphuryl chloride, phosphorus oxychloride and antimony pentachloride, when in excess, dissolve considerable quantities of tellurium chloride or of the double chloride as the case may be.

Inasmuch as the question of the complexity of tellurium has been repeatedly raised, especially so after the prediction of Mendeléeff in his London address,[1] when he predicted that tellurium contained another element, whose atomic weight would be 212 and which he called dvi-tellurium; and after the work of Brauner,[2] when he thought from some of his experiments that the so-called element was actually a composite, it has been deemed important to examine these mother liquors, arising from the reactions above indicated, to ascertain whether any of the reagents studied would possibly allow of a splitting apart of tellurium.

Norris, Fay and Edgerley[3] studied the elementary character of tellurium by carrying out an elaborate fractional crystallization of the double bromide of tellurium and potassium. Later Norris[4] made fractional distillations of tellurium oxide, following the distillations by determinations of the atomic weight. The conclusions drawn by Norris are that his results have furnished positive evidence in favor of the elementary character of tellurium.

Baker and Bennet[5] have recently published an account of their investigations on the atomic weight and elementary character of tellurium. Their work was carried on for a period of thirteen years. They studied the fractional crystallization of telluric acid, the progressive solubility of barium tellurate, the fractional distillation of the metal, chloride and dioxide, the fractional decomposition of the hydride, the fractional electrolysis of the bromide and chloride and the fractional precipitation of the chloride by water. They have been unable to distinguish any difference in the atomic weight and consider 127.6 to be the true atomic weight.

Study of the Products of the Reaction of Various Anhydrous Chlorides on Tellurium and Its Oxide.—The mother liquor arising from each of the reactions studied was decomposed by water, and the tellurium pre-

[1] *J. Chem. Soc.*, **55**, 649.
[2] *Ibid.*, **55**, 411.
[3] *Am. Chem. J.*, **23**, 105.
[4] THIS JOURNAL, **28**, 1675.
[5] *J. Chem. Soc.*, **91**, 1849.

cipitated from hydrochloric acid solution by sulphur dioxide, after which it was carefully purified from such materials as might be introduced by the reagents used.

In each case the tellurium obtained was found to answer to all of the tests to which the original material responded and behaved in all respects similarly to what we commonly know to be tellurium.

The method of approaching this problem can be illustrated by the experiments in which the action of phosphorus oxychloride on tellurium dioxide was studied. In this case a crystalline compound is found which careful analysis has shown to have the composition $TeCl_4.POCl_3$. The excess of phosphorus oxychloride used was observed to carry considerable quantities of tellurium in solution. This mother liquor was carefully decanted from the crystallized salt and treated with water. By this procedure, the phosphorus oxychloride is converted into phosphoric and hydrochloric acids and the tellurium tetrachloride decomposed into hydrated dioxide.

After addition of sufficient hydrochloric acid to completely dissolve the tellurium dioxide, treatment with sulphur dioxide yielded elementary tellurium. It has been observed in working with this particular liquid that when an attempt is made to precipitate tellurium out of a solution containing a large quantity of phosphoric acid the reaction is very much retarded and the tellurium precipitates very slowly. This can be overcome, in a large measure, by the addition of hydrochloric acid and considerable dilution with water. The retardation of precipitation of tellurium in presence of phosphoric acid is doubtless due to lack of dissociation and the precipitation can better be effected after addition of considerable quantities of hydrochloric acid.

The tellurium, after having been converted into chloride by means of aqua regia, was again precipitated by sulphur dioxide, converted into the basic nitrate and crystallized from nitric acid solution, as has been suggested by Norris, Fay and Edgerley[1] for the purification of tellurium. The basic nitrate, when ignited, gave the dioxide.

Determination of the amount of tellurium in the dioxide by precipitation as element gave the ratio

0.85635 TeO_2	0.6845 Te	127.52 at. wt. Te.

The tellurium thus obtained from the excess of phosphorus oxychloride showed by the ratio of tellurium dioxide to element that no apparent change in atomic weight had taken place, and that no splitting apart of the element had occurred was evidenced by the fact that the salt $TeCl_4.POCl_3$ which did not dissolve in the excess of phosphorus oxychloride, and which contained all of the tellurium not appearing in the

[1] *Am. Chem. J.*, 23, 105.

mother liquor, showed by analysis a rational formula with tellurium taken at the commonly accepted atomic weight.

The mother liquors appearing in all the reactions of the anhydrous chlorides which were brought in contact with tellurium or the dioxide were examined in a manner similar to that with phosphorus oxychloride and the same character of results were obtained. A rational formula for the insoluble crystalline product always appeared when a careful analysis was made, while the tellurium appearing in the mother liquor, after decomposing the excess of reagent and purifying the element from such products of the reaction as might contaminate it, always showed the ratio of tellurium dioxide to element corresponding to the atomic weight of 127.5 for tellurium.

Tellurium and Ferric Chloride.—By heating together in the dry condition tellurium and anhydrous ferric chloride, reaction ensues with the production of ferrous chloride, and tellurium tetrachloride. This reaction can also be accomplished and much more conveniently so by the continued action of a hot solution of ferric chloride on tellurium,

$$4FeCl_3 + Te = TeCl_4 + 4FeCl_2.$$

Pethybridge[1] has studied the action of a solution of ferric chloride having a density of 1.18 on telluride gold ores and claims to be able to extract the tellurium as tetrachloride with the simultaneous formation of ferrous chloride, leaving behind gold and silver as follows:

$$8FeCl_3 + (AuAg)Te_2 = 2TeCl_4 + 8FeCl_2 + (AuAg).$$

This is in line with the results previously obtained by the author,[2] which indicate that the tellurium in the natural tellurides of gold is not strongly united to the gold.

While tellurium reduces ferric chloride to ferrous with the simultaneous production of the tetrachloride, ferrous salts will precipitate a part of the tellurium when added in excess to a solution of the tetrachloride in hydrochloric acid.

Crane[3] and Rose[4] have attributed this precipitation of small quantities of tellurium by means of ferrous sulphate to the presence of tellurium dichloride in the tetrachloride. Tellurium dichloride is, however, decomposed by water or aqueous hydrochloric acid into the element and oxide or chloride, and with the knowledge that tellurium dissolves in hydrochloric acid in the presence of the air to tetrachloride directly, it would seem that the precipitation of small quantities of tellurium by means of ferrous salts is largely controlled by mass action. The re-

[1] U. S. Patent No. 709,037, Sept. 16, 1902.
[2] THIS JOURNAL, 24, 355.
[3] *Am. Chem. J.*, 23, 408.
[4] *Pogg. Ann.*, 21, 443.

actions between ferric chloride and tellurium and ferrous salts and hydrochloric acid solutions of the tetrachloride are indeed reversible.

In view of this partial precipitation of tellurium by ferrous salts, a series of experiments was conducted, in which this partial precipitation was made the basis of a fractionation. To this end a quantity of tellurium originally obtained from the Baltimore Smelting and Rolling Co., was precipitated from a caustic soda solution by means of grape sugar. The carefully washed material was dissolved in aqua regia and was precipitated by sulphur dioxide from a hydrochloric acid solution. The tellurium thus obtained was fused with pure potassium cyanide, the resulting fusion extracted with water and a current of air passed through the solution to precipitate the tellurium out of the solution of the alkaline telluride, leaving sulphur or selenium present in solution as alkaline thiocyanate or selenocyanate. The tellurium purified in this manner was introduced into a porcelain boat which was placed in a porcelain tube. This tube was connected with a supply of hydrogen, which was generated from pure zinc and hydrochloric acid and which was washed with water. The tellurium was distilled from the boat (the tube being heated by a blast lamp) into the cooler portion of the tube where it was condensed. The distilled metal was collected and introduced again into a clean porcelain boat and tube and the distillation repeated.

Twenty-five grams of this metal were dissolved in a mixture of nitric and hydrochloric acids and a hydrochloric acid solution of the tetrachloride formed by boiling off the excess of nitric acid. To this solution was added a solution containing about 25 grams of ferrous sulphate, which contained a small amount of ferric salt, when a precipitate of about 0.1 gram of elementary tellurium appeared. The quantity of precipitate obtained did not appear to be materially increased by the addition of a considerably larger quantity of the ferrous sulphate solution. The solution containing the tellurium and iron salts was treated with acid sodium sulphite and the tellurium precipitated. This tellurium was then reconverted into chloride by means of hydrochloric and nitric acids and ferrous sulphate again added to the hydrochloric acid solution. A second precipitate of about the same size as before, appeared. This operation was repeated twenty-four times, fractions being obtained each time of approximately the same size. These twenty-four precipitates were combined, dissolved in hydrochloric and nitric acids and a hydrochloric acid solution obtained as before. Treatment of this solution with ferrous sulphate again yielded a small precipitate of tellurium, the size of the precipitate being about the same as in the previous series of fractions. A second precipitation was made and was combined with the previous one for an atomic weight determination. The metal was treated with nitric acid in a small Jena flask, and the resulting basic ni-

trate gradually heated to 440°, when the weight was found to be constant.

0.1694 Te gave 0.2119 TeO_2 and if O = 16, Te = 127.55.

Inasmuch as the original material showed the same atomic weight, it is evident that by this method of fractionation no portion can be found which shows a figure radically different from the commonly accepted figure.

Action of Hydrochloric Acid on Tellurium in Presence of Air.—Although tellurium is ordinarily considered as insoluble in hydrochloric acid, yet it is actually attacked slightly by the acid when exposed to the air, if sufficient time is allowed for contact. This action can be demonstrated by bubbling a current of air, for several weeks, through concentrated hydrochloric acid in which is suspended metallic tellurium. In a comparatively short time the acid becomes yellow, indicating the presence of tetrachloride.

This action of hydrochloric acid on tellurium in the presence of air has been made the basis of an experiment in which it would be possible to have differential solution take place should tellurium contain a higher member of the series of elements in which it is commonly placed.

One hundred grams of carefully purified tellurium was precipitated from hydrochloric acid solution by means of sulphur dioxide and the precipitate washed until the wash water would not react for chloride with silver nitrate. This freshly precipitated and finely divided metal was introduced with pure concentrated hydrochloric acid into a filtering flask and a current of air which had been previously washed with water and then passed through pure hydrochloric acid, was drawn through the solution for three months. At the end of this time a considerable part of the metal had dissolved. The solution was filtered and on treatment of the solution with acid sodium sulphite, tellurium was precipitated. Two portions of tellurium were here obtained, one of which was a smaller portion of a few grams obtained from a tellurium solution that had been formed by the slow action of hydrochloric acid and air on tellurium, and this solution had remained in contact with the main part of the finely divided metal for three months. The portion which dissolved and that still remaining undissolved were found to be identical in chemical character, obeyed the same reactions, and when converted into oxide, and this oxide analyzed, gave an atomic weight of 127.5.

In the hands of the author, tellurium has shown no signs of breaking apart in any of the reactions which had for their object a study of the elementary character of the metal, nor in the various reactions or derivatives which have been studied in our laboratory has the element shown any indications of other than simple character.

The statements of Mendeléeff as to the possibility of tellurium contain-

ing another element and his views as to its incorrect atomic weight have led to an extended series of critical studies on this subject. Brauner studied the atomic weight for six years, Norris for nine, Baker and Bennet for thirteen, and the author for ten. We see, therefore, thirty-eight years of experimental work directed to the study of the atomic weight of an element which to-day remains as an element whose elementary character is well established, and which stands with a higher atomic weight than the next element in the horizontal series. While it still remains an exception to the periodic arrangement of Mendeléeff, and so far as its comparison with iodine is concerned, is abnormal, yet in the main points of its chemical behavior and those of its compounds, it properly belongs associated with sulphur and selenium in the sixth group.

The element tellurium still remains, however, an exception to the periodic arrangement of Mendeléeff, its atomic weight being higher than that of iodine. We must hence conclude that either tellurium is abnormal in a direction which has not yet received careful study, or that we do not yet appreciate all of the principles of the periodicity of the elements.

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A STUDY OF THE SOLUBILITY OF POTASSIUM CHLOROPLATINATE.

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The importance of knowing accurately the solubility of a precipitate, in the liquor from which it has been thrown down, if the precipitate is to be used for a quantitative estimation, is apparent to every one. This is the case, in particular, with such substances as potassium chloroplatinate, when this salt is to be used for the determination of the amount of potassium occurring in feldspars and such igneous minerals, where the amount of chloroplatinate which is to be weighed is, generally speaking, comparatively small. The difficulty here encountered is, in a measure, overcome by the methods worked out by Hillebrand[1] and his pupils, who evaporate the solution containing the salt in question, together with the corresponding sodium salt, to dryness and then dissolve out the sodium salt with absolute or eighty per cent. alcohol. The trouble, however, although lessened, is still of the same nature as before, and even under the best conditions some of the potassium salt must be carried into solution, giving a high value to the sodium. With these features of the case in mind, it was thought that it would be of some interest to study the solubility of the potassium chloroplatinate somewhat more carefully than had

[1] Hillebrand, "Analysis of Silicate and Carbonate Rocks," *Bull.* 305, *U. S. Geol. Survey.* Washington: Analysis of Rocks.

hitherto been done, under somewhat similar conditions to those encountered in precipitating this salt from solution in ordinary analytical work. The experiments which have been carried out with this end in view, are described in the following pages.

Bunsen and Kirchhoff[1] were the first to work on the solubility of the chloroplatinate of potassium. They made measurements of its solubility in water, at various temperatures between 0° and 100°. Crookes,[2] when studying the solubility of thallium salts, determined the solubility of potassium chloroplatinate in water at 15° and 100°. Fresenius[3] determined the solubility of this salt in solution of ethyl alcohol and water, which contained 55, 76 and 97.5 per cent. of the alcohol. Gibbs,[4] while working out the separation of the platinum metals, found that "potassium chloroplatinate is insoluble in strong, cold, aqueous solutions of potassium chloride." Precht[5] determined the solubility of this chloroplatinate in absolute alcohol and in 96 and 80 per cent. alcohol-water solutions. He also made some very interesting observations on the preparation of the pure salt. Peligot[6] studied the solubility of the salt in question in solutions of ethyl alcohol and water, and he also made a determination of the solubility in absolute methyl alcohol. No systematic study has been made of the solubility of the chloroplatinate in different concentrations of potassium chloride, nor has the influence of other alcohols been ascertained. It was thought that it would be worth while to obtain some data with regard to both of these points, to somewhat extend the observations mentioned above, and also to ascertain the influence on the solubility of the chloroplatinate of the presence of sodium chloride.

Apparatus.—A constant temperature bath was necessary, in which the solutions could be maintained at a given temperature until they should have attained complete equilibrium. The bath used had a capacity of about 40 liters. It was insulated with a thick coating of felt on the sides, and a thick board of asbestos on the top. It carried the usual arrangement for keeping the solutions constantly agitated, a small hot-air engine of the Hendrici form supplying the motive power for running the stirrer. The bath was supplied with an Ostwald gas regulator, by means of which the temperature could be kept constant, if necessary, within 0.1°.

All burettes and pipettes used were carefully standardized by weighing the water which they delivered.

[1] *Pogg. Ann.*, 113, 372 (1861).
[2] *Chem. News*, 9, 37 (1864).
[3] *Anal. Chem. und Pharm.*, 59, 117.
[4] *Am. J. Sci.* (2), 31, 70.
[5] *Zeit. anal. Chem.*, 18, 509 (1879).
[6] *Monit. scient.* (4), 6, 872 (1892).

The tubes, which contained the solutions while they were in the bath, were of hard glass and had a capacity of about 55 cc. The rubber stoppers used to seal them were boiled in dilute caustic soda for several hours before using, to remove surface impurities.

Two thermometers, A and B, were used in the course of the work, to indicate the temperature of the bath. They were standardized at 0° in a bath of melting ice; again at the transition point of sodium sulphate,[1] 32.383°; and again at 100°.

Preparation of Materials.—The chloroplatinic acid used in preparing the potassium chloroplatinate was prepared as follows: Platinum scrap was boiled for several hours with c. p. concentrated hydrochloric acid, washed with distilled water, and the boiling repeated for about the same length of time with c. p. concentrated nitric acid, to remove surface impurities. After another washing the scrap was dissolved in aqua regia, using only as much of the nitric acid as was necessary to dissolve the platinum. The color of the precipitate formed with the platinum solution and potassium chloride showed that there must have been an appreciable amount of iridium in the platinum scrap. To remove the iridium, advantage was taken of the fact that ammonium chloroiridate is much more soluble in water than ammonium chloroplatinate. 100 parts of water at 20° dissolve only 0.666 part of ammonium chloroplatinate, while 5.00 parts of ammonium chloroiridate will dissolve in 100 parts of water. Accordingly, a somewhat dilute solution of ammonium chloride, that had been once recrystallized, was added slowly, with constant stirring, to the chloroplatinic acid solution, care being taken not to precipitate quite all of the platinum. The ammonium salt thrown down was of a very brilliant yellow color, while the chocolate color of the residue left upon evaporation of the mother liquor, showed that a large part of the iridium had remained behind.

After thoroughly washing the precipitate of ammonium chloroplatinate it was reduced in hydrogen to spongy platinum, and the platinum again dissolved in aqua regia. At this point a slight black residue remained, which would apparently not dissolve in the aqua regia, and which we supposed to be iridium. The solution of the spongy platinum was now precipitated as before with ammonium chloride, the precipitate reduced, the spongy platinum dissolved in aqua regia, and again precipitated with the ammonium chloride. The mother liquor left from this precipitation showed no sign whatever of the presence of iridium, while the residue which was noticed when the first portion of spongy platinum was dissolved did not appear after the second precipitation.

As a further proof of the absence of iridium from the product thus

[1] Richards and Wells, *Proc. Am. Acad. Arts and Sciences*, **38**, 431 (1902).

prepared, one-half of the sample was taken and reduced, the spongy platinum dissolved in aqua regia, and again precipitated with ammonium chloride. The precipitate thus obtained was successively recrystallized three times from water. The mother liquors from these recrystallizations were combined with that from the precipitation, and the whole evaporated. However, no indication of iridium appeared in the solution or in the residue.

The final precipitate of ammonium chloroplatinate, which was now assumed to be free from iridium, was reduced, the platinum dissolved in aqua regia, and this was followed by two evaporations, carried almost to dryness, in the presence of an excess of concentrated hydrochloric acid, to remove all traces of nitric acid. Precht,[1] and later Dittmar and McArthur,[2] and more recently Noyes and Weber,[3] have shown how necessary it is to get rid of all the nitric acid, before precipitating with potassium chloride, if a precipitate of known composition is to be obtained. The residue from the final evaporation was taken up with enough water to give a solution containing about 5 per cent. of platinum, and this was added slowly, with constant stirring, to a dilute solution of potassium chloride.

The potassium chloroplatinate prepared in this way was thoroughly washed and carefully dried at a temperature of about 80°. It was kept over anhydrous calcium chloride until used.

From the analysis of several portions of chloroplatinate prepared in different ways, and from solutions of varying dilution, it appears that there is considerable tendency for the precipitate to carry down with it other substances from the solution. This point is receiving some attention in this laboratory. It is enough to say here that the precipitate obtained as above did not contain an appreciable excess of the platinum or of the potassium chloride.

The potassium chloride used in the above preparation, as well as that used directly in making the solubility determinations, was prepared by dissolving Kahlbaum's chemically pure product in distilled water and precipitating this with hydrogen chloride gas, generated by boiling chemically pure hydrochloric acid. The potassium chloride precipitated in this way was twice recrystallized from water, washed, and dried at a temperature of 110°.

The sodium chloride used was prepared in the same manner as the potassium salt.

Methyl alcohol, free from acetone, was digested for nine hours with a large amount of fresh calcium oxide. It was then distilled. The distillate was treated with a fresh quantity of calcium oxide, and again dis-

[1] *Loc. cit.*

[2] *Trans. Roy. Soc. Edin.*, **33**, 561 (1887).

[3] THIS JOURNAL, **30**, 13 (1908).

tilled. That portion coming over at 65.5° was collected and used in these experiments.

The other alcohols, ethyl and isobutyl, were freed from water in a similar manner. Those portions distilling over at 78.4° and 106°, respectively, were used.

These alcohols, after being dehydrated, were carefully protected from the moist air of the laboratory.

The water used in this work was prepared by distilling the ordinary distilled water of the laboratory, after adding a few crystals of potassium permanganate and a few drops of sulphuric acid. As a further indication of its purity, its electrical conductivity was found to be as low as could be expected.

Measurements.—We will first consider the solubility of the salt in water at different temperatures. The method of procedure was as follows: To the tubes were added about 50 cc. of water, and somewhat more chloroplatinate than would dissolve at the particular temperature at which the determination was to be made. It should be stated here that two different determinations were made for every point investigated. The temperature of the bath was now raised to the required point and the thermostat regulated so as to maintain the water at this temperature. The tubes were now attached to the paddles of the stirring apparatus and constantly rotated for from twelve to twenty-four hours. At the lower temperatures, equilibrium is attained very slowly, and in these cases the stirring was continued over night. Several experiments had shown that the solutions would become completely saturated within this time.

In order to determine how much of the chloroplatinate had been dissolved, after the required time had elapsed the stirrer was brought to rest and a test tube raised in the bath, until the top stood just above the water. When the excess of salt had completely settled, which, with the heavy precipitate we are here concerned with, takes place in a very short time, the stopper was removed, and as quickly as possible 25 cc. of the solution were withdrawn with the calibrated pipette, and first transferred to a tared specific gravity bottle and weighed. This procedure was necessary in order to obtain the data required to express the results in terms of grams of salt dissolved in 100 grams of solvent. This solution was then washed into a weighed platinum dish. After evaporating carefully and drying at a low temperature, the dish and residue were weighed. Further drying of the dish and contents was followed by another weighing, and this treatment was repeated until the weight became constant. This process was repeated with 25 cc. of the contents of a second tube, and we thus had two measurements of the solubility

at this particular temperature. The mean of these two determinations gives the values tabulated below.

The results of the determinations of the solubility of the chloroplatinate in water at different temperatures are shown below in Table I.[1] These values represent the amounts of salt, in grams, soluble in 100 grams of water, all weights being reduced to the vacuum standard. For the purpose of this reduction the specific gravity of the chloroplatinate was taken to be 3.54:[2]

TABLE I.—RESULTS SHOWING THE SOLUBILITY OF POTASSIUM CHLOROPLATINATE IN WATER AT DIFFERENT TEMPERATURES.

Temperature.	Weight of K_2PtCl_6 dissolved.	Temperature.	Weight of K_2PtCl_6 dissolved.
2°	0.4812	59°	2.396
16°	0.6718	68°	2.913
25°	0.8641	78°	3.589
35°	1.132	92°	4.484
48°	1.745		

These results are shown graphically in Plate I, where the temperatures are plotted as ordinates and the weights of chloroplatinate dissolved as abscissae. In order that the results might be compared with those of other observers the amount of salt dissolved for the temperatures 10°, 20°, 30°, etc., taken from the curve in Plate I, are given below, together with those of Bunsen:[3]

TABLE II.—RESULTS COMPARING THE SOLUBILITY VALUES FOR POTASSIUM CHLOROPLATINATE IN WATER, OBTAINED BY PREVIOUS INVESTIGATORS, WITH THOSE OBTAINED BY THE AUTHORS.

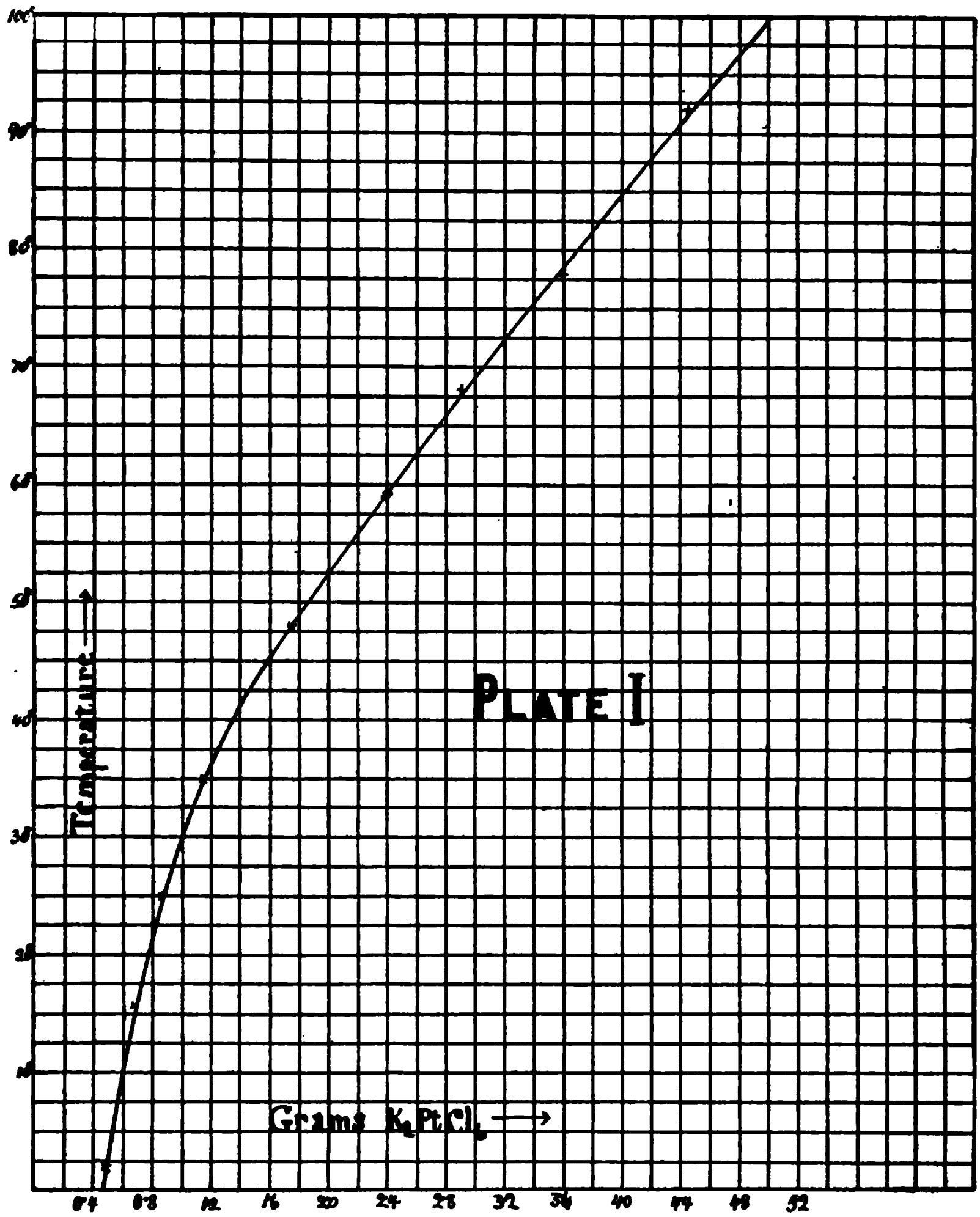
	Weight of K_2PtCl_6 dissolved.			Weight of K_2PtCl_6 dissolved.	
Temperature.	Authors.	Bunsen.	Temperature.	Authors.	Bunsen.
0°	0.4784	0.74	60°	2.444	2.64
10°	0.5992	0.90	70°	3.055	3.19
20°	0.7742	1.12	80°	3.711	3.79
30°	1.000	1.41	90°	4.360	4.45
40°	1.355	1.76	100°	5.030	5.18
50°	1.865	2.17			

[1] It has been pointed out to us by Prof. W. A. Noyes that Dr. Weber found that a solution of potassium chlorplatinate became acid upon boiling. We find that this hydrolysis goes on even at ordinary laboratory temperatures although very slowly, the reaction not being completed within five days. The effect of this reaction upon the solubility appears to be very slight, as a solution of the salt saturated at 95° and maintained at this temperature in contact with the solid phase for 36 hours, upon cooling to 75° gave practically the same value for the solubility as a solution saturated at 75° and not allowed to rise above this temperature. Several of the determinations given in the above table were obtained by approaching the saturation point from both directions. This hydrolytic reaction is being studied further at different temperatures and we hope to have something further to communicate in the near future.

[2] Landolt-Börnstein-Meyerhoffer, Tabellen.

[3] *Loc. cit.*

Crookes[1] states that one part of this chloroplatinate will dissolve in 108 parts of water at 15°, and in 19 parts at the boiling-point of water.



It is at once apparent that the present results show an appreciably lower solubility of the platinum salt in water, particularly at the lower temperatures, than other investigators have found. It seems possible that the salt with which they worked may not have consisted entirely of the chloroplatinate, as Precht,[1] and quite recently Noyes and Weber[1] have shown that it is very difficult to prepare pure chloroplatinic acid. If the nitric acid is to be completely removed by evaporation, this pro-

[1] *Loc. cit.*

cess must be carried out repeatedly, and in the presence of a large excess of hydrochloric acid. Any contamination which resulted from an incomplete removal of the nitric acid would doubtless give high results for the solubility of the chloroplatinate. It is possible, too, that the more complete removal of the iridium in the present instance may also have lowered the solubility slightly.

Before dismissing this point, it should be stated that every care was taken to have the solutions saturated with the chloroplatinate, at the particular temperature at which the experiment was being made, before they were removed from the bath. In some cases they were rotated in the bath for 50 hrs. before being analyzed.

It should be noted that the curve in Plate I is a continuous one over the whole range of temperature investigated.

Solutions of Methyl Alcohol and Water.—Solutions of methyl alcohol and water, as solvents, were next tried, the procedure being much the same as in the previous case, except, that here, four parallel determinations were usually made. As the experiments were being carried on very near the temperature of the laboratory, it was thought better, although perhaps not necessary, to filter the 25 cc. of the solution which had been measured out with the pipette, before evaporating. It was found that when the amount of alcohol in the mixture was as high as thirty per cent., reduction of the chloroplatinate to platinum black took place during the evaporation. This method of determination had therefore to be abandoned. In its place we used a colorimetric method as follows: A standard solution of potassium chloroplatinate in pure water was prepared, containing seven grams of the salt per liter of solution. The unknown solution to be determined was poured into a Nessler tube of 100 cc. capacity and distilled to the mark. Using the standard solution as a basis, another solution was prepared in a second tube, which had the same strength of color as the unknown. The volume of the standard solution required to produce this color, multiplied by the amount of chloroplatinate in unit volume, gave the amount of salt in the original unknown. Care was always taken to have the conditions the same in the unknown as in the known solution. For instance, both solutions always contained the same amounts of alcohol or potassium chloride as the case might be; they were also kept at the same temperature, which was a little higher than the temperature at which the determination was being made. It was found that by this method we could detect the presence of 0.0005 gram of potassium chloroplatinate dissolved in 100 cc. of water, or one part of the salt in two hundred thousand parts of water. It is believed that this method gives a degree of accuracy in the determination of a number of points, in particular those dealing with the dilute solutions, that has not hitherto been reached.

With regard to the mixture of ethyl alcohol and water, as well as those of isobutyl alcohol and water, the determinations were carried out in all respects like those described above.

The results for the solubility of potassium chloroplatinate, in various concentrations of methyl, ethyl and isobutyl alcohol and water, are given in Table III. The measurements were all carried out at a temperature of 20°. In the case of isobutyl alcohol and water only two measurements were made, as this alcohol only dissolves to a small extent in water.

In order that these values might be comparable with those obtained by other investigators, the composition of the solutions is expressed in grams of alcohol per one hundred grams of solution, while the amounts of salt dissolved are given in grams per one hundred grams of solvent. As before, all weights are referred to a vacuum.

TABLE III.—RESULTS SHOWING THE SOLUBILITY OF POTASSIUM CHLOROPLATINATE IN SOLUTIONS OF DIFFERENT ALCOHOLS IN WATER.

Per cent. of methyl alcohol.	Weight of K_2PtCl_6 in 100 gms. solution.	Per cent. of ethyl alcohol.	Weight of K_2PtCl_6 in 100 gms. solution.	Per cent. of isobutyl alcohol.	Weight of K_2PtCl_6 in 100 grams solution.
0.00	0.7742	0.00	0.7742	0.00	0.7742
8.10	0.4434	3.996	0.5258	8.20	0.625
16.55	0.3050	8.08	0.4122	(saturated)	0.318
25.38	0.2188	12.25	0.3325		
34.58	0.1495	16.51	0.2565		
44.25	0.0877	25.30	0.1698		
54.34	0.0478	34.52	0.1088		
70.42	0.0185	44.16	0.0742		
87.7	0.0061	54.3	0.0356		
100.0	0.0027	64.9	0.0199		
		76.0	0.0131		
		87.7	0.0052		
		100.0	0.0009		

TABLE IV.

Values showing the solubility of potassium chloroplatinate in mixtures, made up of even percentage values by weight of water and alcohol. For the sake of comparison, Peligot's results for ethyl alcohol mixtures are given in the last column.

Per cent. of alcohol by weight.	Weight of K_2PtCl_6 in 100 gms. of solution. Methyl alcohol mixtures.	Ethyl alcohol mixtures.	Peligot's results, ethyl alcohol mixtures.
0.00	0.7742	0.7742	0.75
5.00	0.535	0.491	....
10.00	0.412	0.372	0.5
20.00	0.2642	0.218	0.35
30.00	0.1831	0.134	0.28
40.00	0.1165	0.076	0.14
50.0	0.0625	0.0491	0.12
60.0	0.0325	0.0265	0.08
70.0	0.0182	0.0128	0.06
80.0	0.0124	0.0085	0.05
90.0	0.0038	0.0025	0.02
100.0	0.0027	0.0009	

These results are shown graphically in Plate II, the per cent. of alcohol being plotted as ordinates and the amounts of salt dissolved in grams, as abscissae. From this curve the above results (Table IV) are taken for the round concentrations.

A glance at the curves in Plate II shows, at once, that the solubility of the salt in the alcohol water solutions varies in a regular manner with the amount of alcohol present, decreasing gradually as the per cent. of alcohol increases. It should be noted, too, that it is appreciably more soluble in the methyl alcohol solutions than in those of ethyl alcohol. This is true also of the pure alcohols, for the absolute methyl alcohol

dissolves about six times as much salt as the absolute ethyl alcohol. This shows that a more complete precipitation of the chloroplatinate is obtained by using ethyl alcohol than methyl.

Attention should also be drawn to the considerable difference between the solubility of the chloroplatinate in 90 per cent. alcohol and in absolute alcohol. The removal of the last 10 per cent. of water lowers the solubility seven times. This shows the importance of using absolute alcohol in the precipitation of this salt. When sodium chloroplatinate is also present, however, it appears from Morozewicz's[1] work, that solutions containing over 80 per cent. alcohol decompose the sodium salt, precipitating sodium chloride.

Potassium and Sodium Chloride Solutions.—The solubility of the chloroplatinate in solutions of sodium and potassium chloride was next examined. These solutions were prepared by weighing out a certain amount of dry salt, making up to a definite volume, and subsequently diluting this standard by means of carefully calibrated pipettes. The determination of the amount of salt (chloroplatinate) which had passed into solution, was made by the colorimetric method. These determinations were, however, in the case of the sodium chloride solutions, always checked in the following manner. When the solutions were first made up, the amount of platinum salt added, as well as the volume of the solution, was carefully determined. When the solutions were ready to analyze, they were taken from the bath, the stopper removed, and the whole quickly filtered through a previously weighed Gooch crucible, the residue of the chloroplatinate being washed into the crucible with absolute alcohol, this, serving at the same time to wash the mat of the crucible. After carefully drying the crucible and contents, they were weighed. This method gave results which were in close agreement with those obtained by the colorimetric method.

TABLE V.—RESULTS SHOWING THE SOLUBILITY OF POTASSIUM CHLOROPLATINATE IN SOLUTIONS OF POTASSIUM AND SODIUM CHLORIDE.

Concentration of KCl solutions.	Weight of K_2PtCl_6 in 100 gms. of solution.	Concentration of NaCl solutions.	Weight of K_2PtCl_6 in 100 gms. of solution.
0.000	0.7742	0.000	0.672
0.200	0.0236	0.050	0.700
0.250	0.0207	0.100	0.729
0.500	0.0109	0.250	0.758
1.000	0.0046	0.500	0.775
2.000	0.0045	0.750	0.791
3.000	0.0043	1.000	0.805
4.000	0.0042	2.000	0.834
Saturated	0.0034		

The results obtained with the sodium and potassium chloride solutions, are shown in Table V. The concentrations are expressed in terms of

[1] *Chem. Abst. Am. Chem. Soc.*, 1, 972.

gram molecules per liter. The measurements were carried out at 20° in the case of the potassium chloride solutions, and in the case of the sodium chloride solutions at 16°.

These results are shown graphically in Plate III, the concentrations of the solutions, as regards potassium and sodium chloride, being plotted as ordinates and the amounts of chloroplatinate dissolved as abscissae.

If we consider the potassium chloride solutions, we see that the amount of salt dissolved diminishes rapidly as the concentration of the potassium chloride increases, until we reach a concentration of about one gram molecule per liter. From this point on, the increase in the concentration of the potassium chloride has very little effect upon the amount

of chloroplatinate dissolved. This is surely what we would expect. Potassium chloride being, in its aqueous solution, a strongly ionized salt, we have here a high concentration of the potassium ion; in this case the one common to both salts. This will prevent the dissociation of the chloroplatinate, and therefore very little will go into solution. Apparently, by the time we have reached a concentration of about one gram molecule per liter, with regard to potassium chloride, equilibrium is practically established between the potassium chloride undissociated and the potassium and chlorine ions, as the addition of more chloride has little effect on the solubility of the chloroplatinate.

In the case of the sodium chloride solutions, we see that the amount of chloroplatinate dissolved increases as the amount of sodium chloride present increases. This increase is rapid at first, but after a concentration of 0.05 gram molecules of sodium chloride is reached, we see from Plate III that this increase is much smaller and very nearly proportional to the increase in concentration of the sodium chloride. The equilibrium is here between the ionized potassium chloride formed and the dissociated potassium chlorplatinate, thus:

$$2NaCl \rightleftarrows 2\overset{+}{Na} + 2\overset{-}{Cl}$$

$$K_2PtCl_6 \rightleftarrows \overset{++}{K_2} + \overset{=}{PtCl_6}.$$

The more dissociated sodium chloride there is present, the more sodium ions there are to unite with the $PtCl_6$ ions to form undissociated sodium chloroplatinate, and therefore the greater will be the amount of potassium chloroplatinate which will dissolve. This being the case, that portion of the sodium chloride which is dissociated will be largely instrumental in causing the potassium chloroplatinate to dissolve. And this is what we find to be the case. The first portion of sodium chloride added to pure water has a greater effect than later portions, as it almost entirely dissociates, while the same amount added to a concentrated solution has almost no effect.

If we compare the solubility of the chloroplatinate in potassium chloride solutions, with its solubility in the water-alcohol solutions, we see that about the same amount of the platinum salt is dissolved by a solution of potassium chloride containing two gram molecules per liter, as by a water-alcohol solution containing ninety per cent. of alcohol. If then, platinum was being precipitated from a solution, and not potassium, a more complete precipitation of the platinum would be obtained by adding a saturated solution of potassium chloride than by adding absolute alcohol.

The work described in the foregoing pages shows that:

(1) Small amounts of potassium chloroplatinate in solution can be estimated colorimetrically with considerable accuracy. This will be true of any salt which gives the $PtCl_6$ anion, provided the color of the cathion is not such as to interfere.

(2) The chloroplatinate is less soluble in solutions of ethyl alcohol and water than in water solutions of either methyl or isobutyl alcohol. Only 0.0007 gram of the salt dissolves in 100 cc. of ethyl alcohol at 20°.

(3) The solubility of the chloroplatinate in potassium chloride solutions decreases with the increase in concentration of the potassium chloride, until a concentration of one gram molecule per liter is reached. Beyond this point, increasing the concentration of the potassium chloride has practically no effect.

(4) The solubility of the chloroplatinate in solutions of sodium chloride, increases rapidly until a concentration of 0.05 gram molecules per liter is reached. For more concentrated solutions the increase in solubility is small and almost proportional to the increase in concentration of the sodium chloride.

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ON A VOLUMETRIC METHOD FOR COPPER.

BY G. S. JAMIESON, L. H. LEVY AND H. L. WELLS.

Received February 26, 1908.

The process to be described is based upon the titration of cuprous thiocyanate with potassium iodate solution in the presence of a large excess of hydrochloric acid. This method of titrating a number of reducing substances, such as free iodine, iodides, arsenites and antimonites, in a very satisfactory manner, is due to L. W. Andrews.[1] The reaction depends upon the formation of iodine monochloride and the disappearance of the iodine color imparted to an immiscible solvent, such as chloroform or carbon tetrachloride.

We find that cuprous thiocyanate is oxidized by iodine chloride sharply and quantitatively with the formation of cupric salts, sulphuric and hydrocyanic acids, according to the equation

$$4CuSCN + 7KIO_3 + 14HCl = 4CuSO_4 + 7KCl + 7ICl + 4HCN + 5H_2O.$$

This oxidation is similar to that obtained in Parr's method[2] for the titration of CuSCN by means of potassium permanganate solution, but we consider the iodate titration far preferable to the latter in simplicity and accuracy.

To show the applicability of the Andrews method to the titration of

[1] THIS JOURNAL, 25, 756 (1903).

[2] *Ibid.*, 22, 685 (1900).

thiocyanates, the following experiments (by L. H. L.) were carried out, using the pure dry compounds and a solution containing 10.706 grams of potassium iodate per liter (1/20 of formula-weight), and titrating in glass-stoppered bottles in the presence of about 5 cc. of chloroform and about one-half of the final volume of concentrated hydrochloric acid.

	Substance taken. Gram.	KIO_3 used. cc.	Substance found. Gram.	Error. Gram.
NH_4SCN	0.1000	39.4	0.1000	0.0000
NH_4SCN	0.1000	39.5	0.1003	+0.0003
AgSCN	0.2000	36.05	0.1995	—0.0005
AgSCN	0.1000	18.1	0.1002	+0.0002
CuSCN	0.2000	57.5	0.1999	—0.0001
CuSCN	0.1000	28.8	0.1001	+0.0001

In some of the above experiments the substance was dissolved before titrating, in a hydrochloric acid solution of iodine monochloride which had been carefully adjusted over chloroform to the colorless point of the latter, but the use of this reagent was found to be unnecessary.

We find that filter paper has no effect upon this titration. This fact permits the use of paper for filtering cuprous thiocyanate in this process. It appears that organic substances are generally inactive towards iodine monochloride, for Andrews titrated tartar emetic directly with accurate results, and we have found by direct experiments that ethyl alcohol, acetic acid, formic acid, and formaldehyde do not interfere with the iodate titration.

The following results were obtained (by G. S. J.) by precipitating cuprous thiocyanate with sulphurous acid and ammonium thiocyanate from a measured solution of copper sulphate of known strength, filtering, sometimes on asbestos, sometimes on paper, and titrating in the manner previously mentioned. Another 1/20 formula-weight potassium iodate solution was used here: 1 cc. = 0.001817 g. Cu.

Copper taken. Gram.	KIO_3 used. cc.	Copper found. Gram.	Error. Gram.
0.0486	26.7	0.0485	—0.0001
0.0486	26.8	0.0486	0.0000
0.0388	21.3	0.0387	—0.0001
0.0351	19.45	0.0353	+0.0002
0.0486	26.7	0.0485	—0.0001
0.0486	26.9	0.0488	+0.0002

In applying the method to ores, we find that lead and antimony, if not removed, will produce high results, but both these metals are removed (to such an extent at least that they do not interfere in the slightest degree) by the evaporation with sulphuric acid in the process which will be described. Silver also must be removed.

For the sake of convenience, we have employed the normal potassium

iodate in the place of the acid iodate used by Andrews. The normal iodate can be purchased in a pure condition (it should be perfectly neutral to test-paper), or it may be easily prepared by the method of Gröger[1] from potassium iodide and potassium permanganate. The salt should be dried at 100° before weighing. We have used, besides the previously mentioned 1/20 formula-weight solutions, one about twice as strong, but for convenience in calculation in determining copper we recommend the use of some multiple of 5.892 grams per liter which gives exact milligrams of copper per cubic centimeter, according to the multiple taken. For instance, with 11.784 grams KIO_3 per liter, 1 cc. = 0.002000 gram copper.

Method of Analysis.—To 0.5 gram of the ore in a 6 oz. flask, add 6 to 10 cc. of strong nitric acid, and boil gently, best over a free flame, keeping the flask in constant motion and inclined at an angle of about 45°, until the larger part of the acid has been removed. If this does not completely decompose the ore, add 5 cc. of strong hydrochloric acid and continue the boiling until the volume of liquid is about 2 cc. Now add gradually and carefully, best after cooling somewhat, 6 cc. of strong sulphuric acid, and continue the boiling until sulphuric acid fumes are evolved copiously. Allow to cool, add 25 cc. of cold water, heat to boiling, and keep hot until the soluble sulphates have dissolved.[2] Filter into a beaker, and wash the flask and filter thoroughly with cold water.[3] Nearly neutralize the filtrate with ammonia and add 10 to 15 cc. of strong sulphur dioxide water. Heat just to boiling and add 5 to 10 cc. of a 10 per cent. solution of ammonium thiocyanate, according to the amount of copper present. Stir thoroughly, allow the precipitate to settle for 5 or 10 minutes, filter on paper, and wash with hot water until the ammonium thiocyanate is completely removed.

Place the filter with its contents in a glass-stoppered bottle of about 250 cc. capacity, and by means of a piece of moist filter paper transfer into the bottle also any precipitate adhering to the stirring rod and beaker. Add to the bottle about 5 cc. of chloroform, 20 cc. of water and 30 cc. of concentrated hydrochloric acid (the two latter liquids may be previously mixed). Now run in standard potassium iodate solution, inserting the stopper and shaking vigorously between additions. A violet color appears in the chloroform, at first increasing and then dimin-

[1] *Z. angew. Chem.*, 1894, 13.

[2] The decomposition and conversion into sulphates here described closely follows the directions of Low, "Technical Methods of Ore Analysis," p. 79, in connection with the iodide method.

[3] With substances containing appreciable amounts of silver a few drops of hydrochloric acid should be added before making this filtration, but not enough to dissolve any considerable amounts of the lead sulphate or antimonic oxide that may be present.

ishing, until it disappears with great sharpness. The rapidity with which the iodate solution may be added can be judged from the color changes of the chloroform.

In order to make another titration it is not necessary to wash the bottle or throw away the chloroform. Pour off two-thirds or three-fourths of the liquid in order to remove most of the pulped paper, too much of which interferes with the settling of the chloroform globules after agitation, add enough properly diluted acid to make about 50 cc. and proceed as before. In this case, where iodine monochloride is present at the outset, the chloroform becomes strongly colored with iodine as soon as the cuprous thiocyanate is added, but this makes no difference with the results of the titration.

In the following experiments (by G. S. J.) weighed quantities of pure copper were put through the above course of analysis in the presence of antimony, and in some cases lead also:

(1 cc. KIO_3 = 0.003610 gram Cu.)

Copper taken. Gram.	Antimony. Gram.	Lead.	Iodate used. cc.	Copper found. Gram.	Error. Gram.
0.1136	0.06	.....	31.35	0.1131	—0.0005
0.0691	0.06	.....	19.05	0.0688	—0.0003
0.0733	0.06	present	20.30	0.0733	0.0000
0.0673	0.06	present	18.75	0.0677	+0.0004
0.0650	0.06	.....	18.08	0.0651	+0.0001
0.0486	0.03	.....	13.50	0.0487	+0.0001
0.0486	0.03	.....	13.48	0.0486	0.0000

Several ores, sulphides, some of which contained lead or antimony, were analyzed by the process (by G. S. J.) in order to compare the results with other methods: (KIO_3 10.706 g. in 1000 cc; 1 cc = 0.001817 g. Cu.)

	Ore taken. Gram.	Iodate used. cc.	Copper found. Per cent.	Copper by other method.
I.....	0.5000	32.2	11.70	11.71 Electrolytic
II.....	0.5000	39.8	14.46	14.50 "
III*a*.....	0.3584	41.2	20.88	20.70 Iodide
III*b*.....	0.2000	22.9	20.80	20.70 "
III*c*.....	0.5000	28.9	20.86	20.70 "
IV*a*.....	0.2000	21.08	19.15	19.02 Electrolytic
IV*b*.....	0.2000	21.10	19.16	19.02 "
V.....	0.2000	20.8	18.89	18.80 Iodide

So far as ease and rapidity are concerned, one of us (G. S. J.) has made in just one hour an analysis of a copper ore, including weighing and calculation, by the method given above. Following Low's[1] modification of the much-used iodide method, the time was one hour and twenty minutes. There is no doubt that the iodate method is the easier and quicker of the two.

[1] *Loc. cit.*

In view of the large excess of potassium iodide employed in the iodide method, it is probable that the iodate method is cheaper.

The potassium iodate solution is perfectly stable and can be preserved without change for years, if protected from evaporation. Ordinarily it is unnecessary to standardize the solution, except by weighing out a known amount of the salt and dissolving it in a known volume. However, should there be any uncertainty in regard to the purity of the salt, or in connection with the relations of the volumetric apparatus, it would be advisable to standardize with pure copper, putting it through all the operations of the process, and thus eliminating also any slight constant errors.

With the precaution just mentioned, the process is capable of reaching a very high degree of refinement, for the method of titration is one of the sharpest and most uniform in its results. Since most of the iodine goes into the small volume of chloroform, the accuracy of the end-reaction is extraordinary.

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SODIUM PEROXIDE IN CERTAIN QUANTITATIVE PROCESSES.

BY S. W. PARR.

Received February 21, 1908.

Sodium peroxide as a reagent in qualitative analysis, described by the writer,[1] has been found, after a number of years of actual service, to have advantages which entitle it to a far wider recognition and a more detailed study for that particular purpose. The same article states "that other properties have developed, mainly of interest in quantitative methods, which it is hoped will be of sufficient value to warrant further notice." It is in connection with this latter phase of the subject that the following processes are offered.

The adaptations of sodium peroxide here referred to are largely the outgrowth of the writer's experience in the use of that substance as a combustion medium for calorimetric determinations. This material has been recognized for some time as a good fusion reagent where both solution and oxidation are to be effected, but the usual methods of fusion in an open vessel are characterized by too great violence and danger of loss as well as by serious decomposition of the containing vessel. By carrying on the fusion in a closed vessel, it is possible to so adjust reagents as to bring about a quiet fusion without spurting. Owing to the concentration of the very great heat within the mass, the walls of the containing vessel must be kept relatively cool by submerging the same in water, thus preventing the corrosion of the container while at the same time there is no interference with the chemical reaction. An idea of

[1] THIS JOURNAL, 19, 341.

the intensity of the heat in the interior of the mass may be gained from the experience occasionally met with of having soft iron wire melted into a round shot. Experiments have been carried on to determine the best conditions for securing a quiet fusion upon substances of widely varying character. In this work a closed cartridge only has been employed. Experiments have been made with bombs of various sizes and of various compositions. A bomb was made of 30 per cent. nickel steel but no special advantage was observed in its use. A bomb of about five times the usual capacity, was also made of the same material but the increase in the charge which this permitted resulted in the development of too great a quantity of heat to warrant its general adoption. In case the walls are melted through, the contact of the molten mass with the surrounding water produces a disturbance with more or less of the characteristics of an explosion. Pringsheim[1] has adapted the method to the determination of the halogens in organic compounds and described a special form of closed crucible for carrying out the process. It is the purpose of this article to make record of a still wider use of the method and to call attention to the adaptability of the bomb which accompanies the Parr calorimeter. It may not have any great advantage over the closed crucible of Pringsheim, but the fact that the bomb is not infrequently already at hand may be a reason for calling attention to it.

Fig. 1 illustrates the bomb in its present form. The ignition is brought about by dropping into the stem a short slug of soft iron or pure nickel wire heated to redness. It will lodge at the valve M, when, by pressing down quickly with the forceps at O, the hot wire is released and drops into the mixture. From the construction of the cartridge it may be seen that, when submerged, the holes in the screw caps provide for the circulation of water about the two ends of the cylinder, thereby permitting the use of rubber gaskets. An air space about the lower part of the cylinder as at E provides for a less rapid cooling of the walls of the chamber than would be the case if the cylinder at that part were in direct contact with the water. The ends of the cylinder are removable and the fused mass is driven ut with a short rod provided for the purpose. A jet of hot water readily washes out the interior surfaces and the entire fusion is thus brought into solution with a minimum amount of water, 50 or 75 cc. being ample.

Fig. 1.

[1] *Am. Chem. J.*, 31, 386.

In applying the process to inorganic substances it is necessary to have a mixture which will carry on the combustion independently of the material under examination. It is also true that many organic substances require, for complete combustion, conditions not provided by sodium peroxide alone.[1] Thus, with carbon and hydrogen, the conditions for the reactions are indicated separately by the following equations:

$$2Na_2O_2 + C = Na_2CO_3 + Na_2O;$$
$$Na_2O_2 + Na_2O + O + 4H = 4NaOH.$$

A series of tests for determining the most suitable reagents has resulted in the following mixture, applicable also to inorganic as well as organic substances. For a detailed statement of the action of these reagents, reference should be made to a recent article on "Calorimeter Constants."[2]

STANDARD FUSION MIXTURE NO. 1.

10 grams (1 measure) of sodium peroxide,
0.5 " potassium chlorate,
0.5 " benzoic acid.

A thorough mixing is effected by enclosing the charge in the bomb and shaking; the bomb is then submerged to prevent the melting through of the metal and the red hot slug is dropped through the stem as above indicated. The process is complete in two or three minutes, when the cartridge may be opened and the fusion transferred to a beaker, where the dissolving and boiling out of the oxygen is accomplished in about five minutes more. These are the fundamental conditions for a large class of substances, some of which are detailed as follows:

Sulphur and Arsenic in Pyritic Ores of Iron and Copper.—If to the charge as just described we add 0.25 gram of a pyritic ore, we shall have a complete decomposition of the pyrites along with the combustion, so that within a very few minutes after the weighing and mixing in the cartridge (fifteen minutes at the most, and usually within ten minutes if desired), we may have our sulphur as sulphate in solution ready for precipitation with barium chloride. Nor is accuracy sacrificed to speed, for the total absence of contamination from the sulphur of gas flames is avoided. Moreover, as Hillebrand has shown,[3] with the bulk of the solution measuring 200 cc. to 300 cc. dehydration for the removal of silica is unnecessary. This method, therefore, is especially well adapted to the determination of sulphur in mineral substances, and is greatly to be preferred to the usual Fresenius method. For pyrites, moreover, it has decided advantage over the Lunge procedure. This is especially true in the case of roasts containing small amounts of sulphur and with pyrites containing copper. In all these cases a perfect fusion is secured. Upon

[1] THIS JOURNAL, 29, 1616.
[2] *Ibid.*, 29, 1618.
[3] *Bulletin* 305, *U. S. Geol. Surv.*, p. 160.

boiling, the ferrate is decomposed, precipitating the iron, but a clear solution results upon acidifying. If it is desired to precipitate the copper, it is necessary to make slightly acid and then faintly alkaline with sodium carbonate, since the copper hydroxide is soluble in an excess of alkali. Arsenic, if present, is in the fusion as sodium arsenate and may be determined by any of the accepted methods. In the following tests a pyritic ore with approximately 10 per cent. of copper was used. The arsenic was determined for comparison by the distillation method.[1] A parallel fusion was also made, using a known quantity of pure arsenic trioxide and copper oxide.

TABLE I.—DETERMINATION OF SULPHUR IN ORES BY FUSION WITH SODIUM PEROXIDE.

Material.	Fusion with Na_2O_2.	Lunge's method.
Galena	14.59	13.83
Zinc blende	29.28	28.73
Arsenical pyrites	29.32	28.52

TABLE II.—DETERMINATION OF ARSENIC BY FUSION WITH SODIUM PEROXIDE

Material.	Arsenic found volumetrically calculated to As_2O_3.	Arsenic found gravimetrically as As_2O_3 and calculated to As_2O_3.	Arsenic present as As_2O_3.
As_2O_2 + CuO	100.3	....	100.0
As_2O_3 + CuO	....	99.97	100.0
Arsenical ore with iron and copper pyrites (a)	11.42	....	11.37
Arsenical ore with iron and copper pyrites (b)	11.68	....	11.43

Sulphur in Coal, Coke, Ashes, Etc.—In the case of coal and coke, the method has very decided advantages over the usual Eschka process. With coal and coke, one-half gram of these substances should be taken and the benzoic acid omitted from the fusion mixture. In ashes, however, the fusion is affected by the use of the benzoic acid, as above described. If desired, the fusion will easily allow the use of from one-half to one gram of ash material. For sulphur in coal and coke, Sundstrom[2] has described a special crucible based on the reaction with sodium peroxide, as suggested by the use of that material for calorimetric purposes. Von Konek[3] makes direct use of the bomb as provided for calorimetric determinations. Both of these writers, with still others, give comparative data showing the satisfactory nature of the results. By use of the fusion mixture, as above given, a much wider range of substances is covered, including those with little or no ability to carry on the combustion by themselves.

By reference to Table I, it will be seen that the results for sulphur in mineral matter are slightly lower by the Lunge method. This is a natural result of the methods employed, since the fusion process gives

[1] *Z. anal. Chem.*, 21, 266.
[2] THIS JOURNAL, 25, 184.
[3] *Z. angew. Chem.*, 1903, 516.

the total sulphur, including any sulphates present. In case of high iron, it is, of course, removed by filtration before precipitating the sulphur.

Sulphur in Rubber.—Rubber may be completely oxidized if brought to a reasonably fine state of division. This may readily be accomplished by grating the rubber on a new file, though the purer grades may be better cut into small pieces with a sharp knife. One- or two-tenths of a gram with the standard charge will give a perfect combustion. The precipitation of sulphur as a sulphate is carried on in the usual manner.

TABLE III.—SULPHUR IN RUBBER.

Material.	Amount taken. Gram.	Method.	Sulphur from peroxide method. Per cent.	Eschka's method.
"Ebonite" rubber packing.....	0.1	10.0 g. peroxide 0.5 g. chlorate 0.3 g. benzoic acid	(a) 4.39	4.32
			(b) 4.30	4.41
White soft rubber tubing.....	0.1	same	(a) 0.98 (b) 0.92	

Halogens, Sulphur, Etc., in Organic Compounds.—As a substitute for the Carius method for decomposing organic compounds of the halogens, the method is in every way to be preferred. It is applicable also to organic compounds of sulphur, phosphorus, arsenic, etc. Pringsheim[1] also refers to this use of sodium peroxide as a qualitative reagent and gives details for carrying out the combustion process. Our own experience proves that, with organic compounds a simple modification of the standard charge is sufficient in that the sum of the material under examination plus the benzoic acid should equal the usual amount of combustible, *viz.*, 0.5 gram. That is, if 0.2 gram of an organic substance such as aniline hydrochloride is taken, the amount of benzoic acid should be 0.3 gram. However, these quantities are flexible within certain limits, though the total amount of organic combustible should not greatly exceed 0.5 or 0.6 gram.

Since, with the halogens, it is necessary to avoid the use of chlorine compounds, the fusion reagents, potassium chlorate and benzoic acid, above given, may be replaced by a mixture made up as follows:

BORO MAGNESIUM MIXTURE.

	Parts.
Boric acid in fine powder.....	5
Potassium nitrate, powdered.....	4
Magnesium, powdered.....	1

The amount of the above boronitrate-magnesium mixture may be increased from 0.5 to 2 grams or until a satisfactory combustion is secured by means of the increased quantity of metallic magnesium present. The charge, therefore, for this class of compounds would be:

[1] *Am. Chem. J.*, 31, 386; *Ber.*, 37, 2155.

FUSION MIXTURE NO. 2.

10 grams (1 measure), sodium peroxide,
1 to 2 grams boro-magnesium mixture,
0.3 to 0.5 gram carbon compound.

In the case of organic substances that are liquid at ordinary temperatures, the conditions are not altered except with very volatile substances where an exact weight is difficult to obtain. For such material a very light bulb of glass is blown from thin-walled tubing of about two or three mm. caliber. This is fused off with a capillary stem and weighed. With care, it is not difficult to make bulbs of one-half inch or more in diameter, weighing less than 0.2 gram. When so made, they may be easily broken after the charge is made up and the cartridge closed. About 0.2 or 0.3 gram of liquid is drawn into the bulb and the capillary placed in the cartridge directly upon the bottom and the standard charge with No. 1 or No. 2 placed above it. After closing the cartridge, a sharp rap on a solid desk will break the glass, when, by shaking, a thorough mixture is secured. This procedure has given good results with benzene and similarly volatile materials.

TABLE IV.—CHLORINE BY FUSION WITH SODIUM PEROXIDE.

Material.	Fusion mixture.	Found as AgCl.	Theoretical.
Sodium chloride.....	Fusion mixture No. 2	60.48	60.60
Aniline chloride.....	Fusion mixture No. 2	27.63	27.36

Carborundum.—Finely divided carborundum burns readily by use of fusion charge No. 2. The carbon in this fusion may be determined volumetrically. In a separate sample, however, the metallic iron should be determined by extracting the same with a magnet and the free silica may be determined by volatilizing with hydrochloric acid, since the silicon of the carbide is not attacked by that reagent. The total silicon from the fusion should then be corrected to ascertain the amount in combination as SiC.

TABLE V.—ANALYSIS OF CARBORUNDUM.

Constituents.	Method.	Per cent.
SiO_2.....	Volatilized with HF	8.27
Iron as Fe.....	Removed by magnet	4.37
Silicon as Si.....	Fusion mixture No. 2	63.58
Carbon as C.....	Volumetric from fusion mixture No. 2	23.67

While various other substances have been tested with satisfactory results such as shales, fire clays, titanium, ores, etc., it is thought that the above descriptions cover a sufficiently wide range of material to indicate the uses to which the method may be put.

I am indebted for analytical results to six or eight senior and graduate students of this department who have from time to time worked with

the methods as indicated. Special acknowledgment should be made to Mr. F. W. Gill for results on arsenic, chlorine and carborundum.

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THE COMPARATIVE OXIDIZING POWER OF SODIUM PEROXIDE AND ITS USE IN QUALITATIVE ANALYSIS.

BY D. F. CALHANE.

Received February 12, 1908.

The detection of chromium in qualitative analysis rests on its oxidation to the chromate and the precipitation of chromate of lead in acetic acid solution. The oxidation is usually effected by chlorate of potash on the solution of chromium hydroxide in strong nitric acid. If by any chance the nitric acid chosen is not strong enough or has become diluted, the oxidation will not occur and the test fails. It is necessary for success that the hydroxides possibly containing iron, aluminium and chromium be freed of water as much as it is possible by drying them quickly by heating. In this part of the procedure the student usually fails to work properly, not enough water is removed, and the subsequent oxidation does not occur. As I have found, in teaching classes in this subject, so much trouble in getting the student to properly observe precautions, it seemed of advantage to apply a test which would be effective and not so much dependent on a certain set of conditions.

Some experiments were accordingly made on the action of certain other oxidizing agents. Among these were chosen sodium peroxide and bromine water. The preference was for the former, as it is to be obtained in a convenient solid form, and possesses few of the disagreeable features of bromine water. A 0.1 N solution of chrome alum was prepared, each cubic centimeter holding 0.0332 g. of chrome alum, answering to 0.005 g. of Cr_2O_3. Next, the oxidation of portions of this solution with peroxide of sodium and bromine water was carried out to see what the comparative efficacy of these two reagents is on solutions containing known amounts of chromium. In this connection an interesting feature in the action of sodium peroxide on chromium solutions was met with, that at first led to the belief that bromine water was more efficient. The dilutions were carried to the point where the amount of chromic oxide present was only 0.000125 g., corresponding to 0.000085 g. of chromium. At this extreme dilution, a safe test was secured with bromine water, but the sodium peroxide apparently failed at a concentration answering to 0.00025 g. chromic oxide. The bromine water appeared to act equally well both hot and cold at all the different concentrations from 0.005 g. chromic oxide down to 0.000125 g. With the sodium peroxide there was no test with the presence of 0.005 g.

chromic oxide, if the solutions were treated cold. When the sodium peroxide was added to the hot solution a small amount of yellow precipitate was obtained. An explanation of this surprising fact was arrived at later.

The next procedure was to find out what the limit of delicacy for the test is in actual analysis. Normal solutions of aluminium nitrate and ferric chloride were prepared, one cubic centimeter of which answered to 0.071 g. aluminium nitrate and 0.054 g. ferric chloride, giving a precipitate of 0.026 g. aluminium hydroxide, 0.0356 g. ferric hydroxide, and 0.0033 g. chromic hydroxide from 1 cc. of the chrome alum. The analysis in the first instance was carried through with a mixture of 1 cc. of each of the three solutions. The aluminium and iron here exceeded the chromium in the ratios of 8 and 12 times, respectively. The solution of the mixed salts was treated with 10 cc. of barium carbonate emulsion and allowed to stand for 2 or 3 minutes. Next a filtration was made, and the filtrate tested for iron, chromium and aluminium. The tests proved complete precipitation of the metals. The barium carbonate residue was dissolved in hot hydrochloric acid. The hydroxides of the three metals reprecipitated with ammonia. These were dissolved in hydrochloric acid and the diluted solution divided into two equal parts. There could be present in each part the equivalent of 0.0025 g. chromic oxide, answering to 0.0016 g. chromium hydroxide. One part was added to a large excess of bromine water, after previously having added excess of sodium hydroxide. After filtration from the iron, no test for chromium appeared on adding acetic acid and lead acetate. In the other portion similarly treated, using sodium peroxide as the oxidizing agent, a good test was obtained. Next, the above procedure was repeated, using 2 cc. of the iron and aluminium solutions and 1 cc. of the chromium. The ratios here were 24 iron, 16 aluminium to 1 of chromium hydroxide. Here again the bromine water failed to act sufficiently for a test, while the sodium peroxide gave a good test. In the third experiment 5 cc. each of the iron and aluminium solutions were taken and 0.5 cc. of the chrome alum solution. After proceeding as before, the bromine water failed to give a test, while 0.5 g. sodium peroxide gave a reliable indication. The ratios here were 81 aluminium and 111 iron to 1 of chromium. The mixed precipitate contained 0.130 g. aluminium hydroxide, 0.178 g. ferric hydroxide, and 0.0016 g. chromium hydroxide. In each of the last two tests the maximum amount of chromic oxide present for oxidation was 0.0008 g., corresponding to 0.0005 g. chromium.

In the next experiment it was desired to contrast the delicacy of the usual method with potassium chlorate and nitric acid with the peroxide procedure. Amounts taken were 5 cc. aluminium nitrate, 5 cc. ferric chloride, and 0.5 cc. chrome alum. The analysis was carried through

in the usual way and the precipitate of iron, chromium and aluminium hydroxides given by ammonia was dissolved in strong nitric acid and boiled with potassium chlorate. The solution was divided into two equal portions and one tested with sodium hydroxide acetic acid and acetate of lead. The result was negative for chromium. Here, as in the previous cases, 0.0008 g. of chromium hydroxide was present. The result shows that the limit of successful oxidation by this method has been exceeded. The time required to carry this out is longer and the test is much less delicate than with the peroxide method.

Another test was made to compare the fusion method of oxidation with that using bromine water, potassium chlorate and nitric acid and sodium peroxide. The usual method of fusing the hydroxides of iron, chromium and aluminium mixed with dry potassium nitrate and sodium carbonate on platinum was followed, having present the same amount of chromium, iron and aluminium as in the previous cases. The result here for chromium by the usual test as lead chromate after oxidation, was surprisingly convincing. Five cubic centimeters of the ferric chloride aluminium nitrate and 0.5 cc. of the 0.1 *N* chrome alum solution were precipitated by ammonia. The precipitate was filtered, washed and fused in a platinum crucible with potassium nitrate and sodium carbonate mixture for a few minutes. The cooled mass was lixiviated with hot water. The iron was filtered off and one-half of the clear filtrate, which was decidedly yellow, was made acid with acetic acid and lead acetate added. A good yellow color was produced due to the formation of lead chromate. This test appears to be equally delicate with the sodium peroxide method. There was present in this fusion test 0.0008 g. chromic oxide, or 0.0005 g. chromium.

In the experiments having to do with the oxidation of the pure chrome alum solution with bromine water and peroxide, it was surprising that the peroxide apparently failed to oxidize the chromium at a concentration where bromine water gave excellent results. It was found, however, that if the solution was hot during the test a very slight precipitate of lead chromate was obtained with the sodium peroxide procedure. Bromine water acted equally well in hot or cold solution. It has been previously shown that in actual analysis sodium peroxide is by far the more powerful oxidizing agent.

It was found on further experimentation that whereas a solution of bichromate was readily oxidized to perchromate by barium peroxide in acid solution, a chromic salt gave no indication of oxidation to the perchromate by the above agent. The chromic salt was only slightly oxidized to the chromate.

Sodium peroxide acting on a solution of the chromic salt gave a yellow color. On acidification a violet color appeared, which concentrated

in ether indicated perchromic acid. In acid solution sodium peroxide gave no such oxidation. If a chromic salt were oxidized by sodium peroxide as above, the solution acidified with acetic acid and lead acetate added, in dilute solutions such as were used in this work, no precipitate appeared. On allowing the solution to stand, or more quickly, on warming, the customary yellow precipitate of lead chromate appeared and oxygen continued to be evolved for some time.

These results show the reason of the failure to obtain the tests for chromate of lead in the earlier part of the work where dilute solutions of chrome alum were severally treated with sodium peroxide and bromine water. The sodium peroxide forms an alkaline solution with the evolution of oxygen. The chromic salt is oxidized to the perchromate, the sodium salt being formed in the alkaline solution. This substance is stable and gives a yellow color to the solution. On acidification with acetic acid, lead acetate produces no precipitate, as the lead perchromate is soluble in this medium. On standing or warming, oxygen is given off and the lead perchromate breaks down to the chromate, giving the customary yellow precipitate.

Oxone, the fused form of sodium peroxide, acts the same as the unfused variety, as would be expected. For analytical work it is less desirable, owing to the impurities it contains. In addition to the silica found in the unfused variety, it carries about 1.5 per cent. of copper as the result of several analyses showed. In addition, small amounts of iron were found to be present. The results obtained in this investigation show that sodium peroxide is the best oxidizing agent for chromium in solution. Sodium perchromate is formed by this agent in alkaline solution. This solution is stable, and, on acidification, oxygen is rapidly and continuously evolved. The oxygen can be liberated as fast as desired, thus giving a powerful oxidizing source simply controlled.

The properties of this alkaline perchromate solution will be further investigated.

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THE DETERMINATION OF CARBON IN STEEL, FERRO-ALLOYS, AND PLUMBAGO BY MEANS OF AN ELECTRIC COMBUSTION FURNACE.

BY C. M. JOHNSON.

Received March 3, 1908.

Several months ago it occurred to the writer that the Hoskins resistance wire could be applied to the heating of combustion tubes. A drawing was prepared for a furnace of a muffle type to heat four tubes lying in the same plane and parallel.

After some correspondence it was agreed, at first, to try a single tube furnace. It consists of a steel tube 295 mm. x 76.3 mm. containing a non-conducting packing of magnesia oxide. In the center is a quartz tube wound with the Hoskins wire.[1] Inside of this tube is placed another of the same material of 19 mm. inside diameter and 600 mm. long, in which the combustions are made.

A. Mercury pressure gauge for detection of leaks and stoppages.
B. Jar for stick potassium hydroxide or for any solid dryer or absorbent.
C. Safety jar for potassium hydroxide solution, preventing solution from backing over into rubber tubing.
D. Calcium chloride jar.
E. Soda lime jar.
F. Mercury valve, to prevent reverse action.
G. Electric combustion furnace.
H. Jar for granular zinc to remove
Acid fumes,
Litharge fumes,
Sulphur fumes,
Chlorine fumes.
I. Jar for phosphoric anhydride to remove water.
J. Absorbent and weighing apparatus for carbon dioxide.

This furnace was to be durable, if not heated above 1100°, but it burned out in three days. It was then rewired with greater resistance and was guaranteed, if not heated above 1000°. Fearing the furnace might again desert the cause, the writer put in a small 32-ohm rheostat that happened to be at hand. With about one-fourth of this resistance the furnace, on a 220-volt direct current, has been maintaining a constant temperature. To secure complete combustion of steel, it is very essential that the heat be maintained as close to 950° as possible, *i. e.*, as little under that temperature as practicable. If the temperature drops to about 900°, or under, the results obtained are liable to be from 0.01 to 0.10 per cent. too low, unless red lead is mixed with the drillings. Hence, if one

[1] The apparatus can be supplied by the Scientific Materials Co., of Pittsburg.

desires to operate with oxygen alone, the necessity of keeping the temperature from 940° to 960° centigrade cannot be made too emphatic.

The oxygen is purified by passage through jars of stick caustic potash, potassium hydroxide solution, calcium chloride, and soda lime in the order named. The oxygen then passes through a mercury valve into the porcelain or quartz (fused silica) tube, half of which is filled loosely with ignited asbestos. The products of the combustion are purified from acid, sulphur, litharge, or chlorine fumes by passing through a jar of granulated 30-mesh zinc. The water is removed by a jar of phosphoric anhydride.

For steels containing 0.30 to 1.50 per cent. carbon two grams of fine drillings, not over one-fourth mm. thick, are taken. For still lower percentages of carbon 3.0 to 5.0 grams of drillings of not over 20-mesh size are selected.

The sample is weighed into a clay boat. (The boat is molded and burned in the laboratory by a boy at a trifling cost.) The steel begins to burn by the time the stopper of the combustion tube is in place. Two grams of steel are decarbonized in three minutes and five grams in six minutes. The burning is continued for ten minutes more with oxygen passing through the combustion tube at a rapid rate. The weighing apparatus is detached, wiped and weighed. Twenty-five minutes afford ample time for a single combustion, counting all operations.

The weighing apparatus and the jars for the purifying train are the writer's design and were first published, in part, with illustrations in the January *Journal of the Engineers' Society of Western Pennsylvania*, 1906, and more fully in THIS JOURNAL, **28**, 862 (1906). This weighing apparatus (J) is used forty times before it is refilled. As it is always weighed against a duplicate for a tare, after the fortieth combustion its tare is used as an absorber for forty more combustions, so that when a pair has been freshly filled the operator knows he can complete eighty combustions before he needs to refill his weighing outfit.

While no red lead is necessary for steel combustions, some of the alloys such as ferro-chrome, carbonless chrome, and ferro-boron, require that red lead be mixed with the drillings or powder to break the metallic bond and permit of decarbonization. Ferro chrome is the most refractory as from a carbon content of more than 4 per cent. only 0.2 per cent. was obtained by burning as in steels with oxygen alone, at a temperature of 940°. Pig-iron also requires some red lead. In general, about one-half the amount of lead required for decarbonization in a gas furnace is sufficient for the same work in the electric furnace, by reason of the higher heat attainable within the range of durability. A few of the many comparisons made in this laboratory between the combustions in

a gas furnace with red lead and oxygen and combustion in oxygen alone are given in Table I:

TABLE I.

Sample.	Method.	Weight of drillings taken.	Amount of red lead used.	Per cent. carbon found.
No. 1 Steel.....	Electric	4 grams	none	0.09
" 1 "	Red lead	4 "	7 grams	0.09
" 288 "	Electric	2 "	none	1.176
" 288 "	Red lead	2 "	4 grams	1.175
No. 2 Steel.....	Electric	5 grams	none	0.121
" 2 "	Red lead	4 "	7 grams	0.111
" 3 "	Electric	1½ "	none	0.976
" 3 "	Red lead	1½ "	4 grams	0.967
" 4 "	Electric	3 "	none	0.109
" 4 "	Red lead	5 "	7 grams	0.118
" 5 "	Electric	2 "	none	0.469
" 5 "	Red lead	2 "	4 grams	0.474
" 6 "	Electric	2 "	none	0.736
" 6 "	Red lead	2 "	4 grams	0.737
" 7 "	Electric	3 "	none	0.118
" 7 "	Red lead	4 "	7 grams	0.117
" 8 "	Electric	2 "	none	1.17
" 8 "	Red lead	2 "	4 grams	1.168
" 9 "	Electric	2 "	none	1.15
" 9 "	Red lead	2 "	4 grams	1.16
" 10 "	Electric	5 "	none	0.046
" 10 "	Red lead	4 "	7 grams	0.040

TABLE II.—FERRO-ALLOYS AND PLUMBAGO.

Sample.	Method.	Weight of drillings taken.	Amount of red lead used.	Per cent. carbon found.
Tungsten powder.....	Electric	2 grams	none	0.003
	Red lead	2 "	4 grams	0.010
Plumbago, No. 153.....	Electric	0.3 "	none	50.700
	Red lead	0.2 "	4 grams	50.800
Plumbago, No. 356.....	Electric	0.3 "	none	51.650
	Red lead	0.2 "	4 grams	51.300
Plumbago, No. 1.....	Electric	0.2 "	none	94.900
	Red lead	0.3 "	4 grams	94.300
68.5 per cent. Ferro-chrome	Electric	1.0 gram	1 gram	4.21
	Red lead	1.0 "	4 grams	4.15
Ferro-vanadium, No. 134.	Electric	1.0 "	none	3.12
	Red lead	1.0 "	4 grams	3.09
Ferro-titanium, No. 1.....	Electric	2.0 grams	none	0.22
	Red lead	2.0 "	4 grams	0.24
Ferro-boron, No. 1.....	Electric	1.0 gram	1 gram	1.73
	Red lead	1.0 "	4 grams	1.72
Carbonless chrome No. 9—	Electric	1.0 "	1 gram	0.08
96.0 per cent. chromium—	Red lead	1.0 "	4 grams	0.09
Pig iron.....	Electric	1.0 "	none	3.20
"B".....	Electric	1.0 "	0.5 gram	3.58
	Red lead	1.0 "	4 grams	3.58

The advantages of the electric heating apparatus are obvious. Very little heat is radiated; economy of space is attained; tubes are heated gradually and cooled gradually; time required is the minimum; labor cost is plainly the lowest because of simplicity and rapidity and no expensive platinum tubes or boats or crucibles are used.

Some may say, "Why not burn the steel in air?" The answer is that the cost of oxygen is small, 1/3 cent per combustion, and the steel burns twice as fast. Oxygen can now be had at 5 c. per cu. ft. in 100 cu. ft. cylinders. The method is accurate for all steels. As pointed out in the writer's article in THIS JOURNAL[1] and in his preliminary paper read before the Pittsburg Section in Dec., 1905, one may lose as much as 50 per cent. of the carbon in certain alloy steels by attempting to dissolve the borings in either neutral or acid double chloride of copper and potassium.

The best protection for the bottoms of clay or porcelain boats is a liberal layer of ignited silica sand, such as is used for acid open-hearth furnace bottoms. The silica rock is crushed to about 20-mesh and ignited in a muffle furnace at a bright red heat, cooled, and kept in glass-stoppered bottles.

To secure complete decarbonization it is necessary either that thin drillings be used or, if the sample contains much coarse or bulky material, it should be selected. This can easily be accomplished by pouring the borings on a 20-mesh sieve and shaking all of the steel of 20-mesh size and the still more finely divided dust on to a 60-mesh sieve, which retains only the 20 to 60-mesh material. This *always* represents a good average sample.

Further, the drillings should be placed in as compact a mass as possible. If curly drillings are scattered along the entire length of the boat instead of being put in a deep, compact body, borings that are a little thick will frequently be found to still contain unburned metal. This detail is a very important one. Of course, the reason is that drillings lying in close contact heat each other to incandescence during the burning with oxygen.

Also, during the period when the oxygen is being absorbed in large quantity by the burning metal, the flow of the gas should be regulated so that there is a bare excess and no more. That is, the oxygen should be turned on in sufficient quantity that the gas is bubbling through the weighing apparatus slowly. If the gas is rushed through during this period the steel becomes violently heated and slags with the sand and the sides of the boat, destroying the latter. Worse yet, low results are obtained frequently in this way, probably due to the formation of carbon

[1] *Loc. cit.*

monoxide, which is driven out of the hot portion of the tube before it is oxidized to the dioxide.

If the oxygen is turned into the tubes in sufficient quantity to maintain a slow stream during the period of the burning, the end point of the combustion is distinctly shown by a sudden increase of the speed of the bubbling through (J). The rush of oxygen is then checked but the rate of flow is still rather rapid for the final ten minutes.

The weighing apparatus (J) is filled not quite to the bend of the inlet tube with a solution of potassium hydroxide made by dissolving 500 grams of the latter in 500 cc. of water. The drying tube at the outlet of J is closely filled with pieces of stick caustic potash cracked to about half the size of a grain of wheat. To prevent the caustic potash from coming in contact with the small rubber stopper in the drying tube a *loose* plug of asbestos is placed at that point. The little bulb of this drying tube is filled about half full of glass wool. If dry sticks of caustic potash are cracked quickly, the small pieces can be conveyed to the drying tube in dry condition and constitute not only a splendid guard against loss of moisture from J but are also equally effective as an absorbent of carbon dioxide.

If a porcelain boat is used, the 15 x 75 mm. Royal Meissen boat is the best shape and most endurable of any porcelain boats that the writer has tried. When putting in the sand bottom, fill the front half of the boat about two-thirds full and then with the butt end of the forceps make a trough in the sand, working it well up the sides of the boat. Pour the drillings from the weighing bottle into this depression. By so doing the drillings are kept in a compact mass and when the combustion is completed the burned steel can be lifted out in a small cake. In this way a boat can be used ten to fifteen times.

When a great many combustions are made daily, the fused silica, or electro quartz, tube is the most durable. The continuous spraying of oxides against the walls of a porcelain tube weaken it and when the current is turned off and the tube is permitted to get cold the contraction causes a rupture.

To prevent the contents of D, B, E from clogging the inlets and outlets, large plugs of cotton are used at these points. Glass wool plugs should be used in H and loose plugs of ignited asbestos in I. Enough mercury is placed in the bottom of F and A to form a seal. The inlet end of the quartz tube heats somewhat and it is better to wrap it several times around with a strip of cheese-cloth, the end of which dips into a 150 cc. beaker of water suspended directly underneath by means of copper wire. During the absorption of carbon dioxide the outlet of J is protected from ingress of moisture or carbon dioxide or fumes from the

room by a drying tube not shown in the figure. It is filled with pieces of stick caustic potash broken to the size of a pea.

LABORATORY OF THE PARK STEEL WORKS,
CRUCIBLE STEEL CO. OF AMERICA,
PITTSBURG, PA.

(CONTRIBUTION FROM THE OFFICE OF PUBLIC ROADS, U. S. DEPT. AGRICULTURE.)

THE EXTRACTION OF POTASH FROM FELDSPATHIC ROCK.[1]

BY ALLERTON S. CUSHMAN AND PREVOST HUBBARD.

Received March 4, 1908.

The extraction of potash from native rocks has long been considered one of the most important as well as one of the most difficult problems of industrial chemistry. In spite of the enormous resources of the North American continent, there has not yet been found anywhere on it an available source of potash, thus necessitating the importation from abroad of many hundreds of millions of pounds per annum of the salts and compounds of this important substance. One result of this lack of a native source of supply has been to stimulate the use in agriculture of hard wood ashes, which are even at the present time brought from Canada in considerable quantities to the added devastation of the fast disappearing forests. In addition to this, cotton hull ashes from the South are shipped to the North, which merely robs the soil of one portion of the country to supply the deficit in another. The pegmatitic granites and feldspathic dykes of the eastern and central western United States offer an unlimited source of supply which only awaits an economical method for making it available. Many of these feldspar deposits run as high as 10 per cent. in potash (K_2O) and it follows, therefore, that a quarry only fifty feet square and fifty in depth contains about 2,000,000 pounds of this alkali. Under the stimulus of the rapidly growing cement industry, great advance has been made in the last few years in the art and economics of fine grinding, which must of necessity be the first step in any process which attempts the extraction of potash from feldspar or other minerals. At the present time, in the manufacture of Portland cements, at least two extremely fine grindings as well as a burning at a high temperature are accomplished so economically that the finished product can be packed in bags or barrels and sold in some places for a price equal to about three-tenths of a cent per pound or about six dollars per ton. In view of the fact that a short ton of 10 per cent. feldspar contains about ten dollars' worth of potash at prevailing prices the problem of extraction is not on first thought an unpromising one from an economical standpoint.

There are about twenty well defined rock-forming minerals as com-

[1] Paper read before the N. Y. Section, Am. Chem. Soc., Feb. 7, 1907. Published with the permission of the Secretary of Agriculture.

prised in the following tabular list, only a few of which, however, may be considered as possible sources of raw material. Of these orthoclase and microcline are probably the most important. The potash feldspars occur in large dykes or deposits in various parts of the country, and have been particularly developed in Maine, Connecticut, New York, Pennsylvania and Maryland, where they are mined and ground for use almost exclusively in the ceramic industries. Many of these pegmatite deposits, however, because of insufficient coarseness, too large a percentage of quartz, or too great an abundance of iron-bearing minerals, are unfitted for finer uses and therefore are especially available as a raw material for potash extraction.[1]

POTASH-BEARING SILICATES ARRANGED ACCORDING TO DANA.

ORTHOSILICATES.

Kaliophilite: Silicate of alumina and potash. K_2O, 27.20–29.30 per cent.

Microsommite: Sulpho-silicate of alumina, lime, soda, and potash. K_2O , 6.25–7.82 per cent.

Nephelite: Silicate of alumina, soda, and potash. K_2O, 4.55–7.14 per cent.

Hauynite: Sulpho-silicate of alumina, lime, and soda (potash). K_2O, 0.33–4.96 per cent.

Algerite: Silicate of alumina, magnesia, and potash, and water with some $CaCO_3$. K_2O, 9.97 per cent.

METASILICATES.

Leucite: Silicate of alumina and potash. K_2O, 18.90–21.48 per cent.

POLYSILICATES.

Orthoclase: Silicate of alumina and potash. K_2O, 5.40–15.99 per cent. Constitutes at least 15 per cent. of the earth's crust and occurs in nearly all varieties of acid igneous and metamorphic rocks, as well as in many sandstones, conglomerates, etc.

Microcline: Same as orthoclase, except as to crystal habit.

Hyalophane: Silicate of alumina, baryta, and potash. K_2O, 7.82–11.71 per cent.

Anorthoclase: Silicate of alumina, lime, soda, and potash. K_2O, 2.50–11.90 per cent.

HYDROUS SILICATES.

Muscovite: (White or potash mica) silicate of alumina and potash. K_2O, 6.83–11.10 per cent.

Lepidolite: (Lithia mica) fluoro-silicate of alumina, lithia, and potash. K_2O, 10.78–12.34 per cent.

[1] See *Mineral Resources of the U. S., 1906.* E. S. Bastin.

Zinnwaldite: (Lithia mica) composition like lepidolite but contains iron. K_2O, 10.46–10.58 per cent.

Biotite: (Iron or black mica) silicate of alumina, magnesia, iron and potash. K_2O, 6.18–10.08 per cent.

Phlogopite: (Magnesia mica) silicate of alumina, magnesia, and potash. K_2O, 7.06–10.32 per cent.

Lepidomelane: (Black mica) silicate of alumina, iron and potash. K_2O, 6.06–9.45 per cent.

Roscoelite: (Vanadium mica), silicate of vanadium, iron, magnesia, alumina and potash. K_2O, 7.59–8.87 per cent.

Zeolites: Hydrous silicates of alumina, lime, soda, run from traces to 11.09 per cent. K_2O. The principal potash-bearing varieties are *Phillipsite* (0–11.09 per cent. K_2O), *Chabasite* (0–4.39 K_2O), *Analcite* (0–2.83 per cent. K_2O), and *Natrolite* (0–1.17 K_2O).

The question of the use in agriculture of very finely ground feldspar without any further treatment has previously been discussed by one of us,[1] and systematic experiments are being carried on year by year by the Department of Agriculture in order to test the value of potters' feldspar ground to 200 mesh as a tobacco fertilizer. It has been pointed out that by grinding the spar, either dry or in the form of a slurry with lime, ammonium salts or gypsum, the potash can be made more quickly available to plants.[2] It is an interesting question whether these simple methods could not be developed in order to prepare feldspathic rock for use in agriculture.

The principal representatives of the potash soda feldspar group, orthoclase and microcline, have the composition generally approximating to R_2O, Al_2O_3, $6SiO_2$, in which R may be either potash or soda. It is probable that very few of the large deposits will run higher than 10 per cent. potash and in many the percentage of soda is considerable and presents a decided complication in any scheme of potash extraction.

When in a finely ground condition, orthoclase is not a difficult silicate to decompose and a number of methods have been proposed and successfully carried out on a small scale. None of these have, however, up to the present time developed into successful commercial operations. Water alone, to a slight extent, decomposes feldspar and will extract a small amount of potash from fine-ground orthoclase, but the action is not continuous and soon practically ceases, owing to the accumulation of the resulting decomposition products, which may form new combinations of a more or less insoluble nature and which also protect the active surface area of the particles from continued decomposition. If the insoluble products are removed by abrasion, solution, electrolysis, or other

[1] *Bull.* 104, *Bur. Plant Ind., U. S. Dept. Agr.*

[2] *Bull.* 28, *Office Public Roads, U. S. Dept. Agr.*, p. 16.

means, the action goes further, but in any case the amount of decomposition depends upon the available surface offered by the powder and therefore upon its degree of fineness. This is true of any reaction which is purely a surface one and is a factor which, in many similar cases, deserves more consideration than is ordinarily given it. Some figures have been presented in a previous publication which show the enormous increase in surface area which results from reducing one pound of feldspar in the shape of a solid cube to the condition of the finest possible powder. It has been shown that whereas the original cube would have a surface area of 29.3 square inches, the same material reduced to particles just capable of passing a screen containing 200 meshes to the linear inch would have an area approximately equal to 24,900 square inches. If further reduced entirely to the finest possible powder, the surface area mounts into millions of square inches.[1]

In a previous publication on the decomposition of the feldspars the authors have already discussed to some extent the effect of fineness of grain on the rate of decomposition and have presented certain data in regard to an electrolytic method for extracting the soluble alkalies from ground rock.[2] Some results of a study of very fine powders have also been presented by the authors in a paper on the air elutriation of fine powders in which a laboratory method for separating the very finest powders from coarser particles was described and the relation of fineness to surface area discussed.[3] By means of an apparatus which may be briefly described as consisting of a series of settling chambers through which the powdered spar is forced by air pressure, a number of samples of the material were obtained differing considerably in the relative size of their particles. From microscopic measurements of the average diameter of the largest, smallest and medium-sized particles in each sample, and taking into account the relative proportion of each of these different sizes present, a close approximation was made of the actual surface area presented by a unit weight of powder, by means of the following formula where M_1, M_2, M_3 equal the per cent. of large, medium and small sized particles and l_1, l_2 and l_3 equal their respective diameters:

$$a = 6\left(\frac{M_1}{l_1} + \frac{M_2}{l_2} + \frac{M_3}{l_3}\right).$$

The object of this paper is to present the results of the continuation of these researches, together with a brief review of our own previous work and that of other investigators.

In our former work the decomposition of an impure orthoclase, as

[1] *Bull.* 104, *loc. cit.*

[2] *Bull.* 28, *Office of Public Roads, U. S. Dept. Agr.*

[3] THIS JOURNAL, 29, 4.

procured in bulk from a commercial firm, was studied, no attempt being made, however, to obtain exact measurements of the fineness of the product, although it was found that nearly 98 per cent. would pass through a standard 200-mesh sieve. This material was found, by analysis, to have the following composition and was used in all of the experiments described in this paper:

Silica (SiO_2)	68.29
Alumina (Al_2O_3)	18.27
Potash (K_2O)	9.32
Soda (Na_2O)	3.60
Phosphoric anhydride (P_2O_5)	0.53
Total	100.01

When leached with water, the powder gave a yield of 0.025 per cent. alkalies in solution, although it was demonstrated that a greater amount had actually been produced by the action of the water and that the difference between this amount and that passing into solution had been combined with or absorbed by the insoluble substances also formed. Wet grinding in a ball mill, by which the particles were further broken down and the insoluble products removed by abrasion, produced a yield of 0.32 per cent. alkalies. It was found that the absorbed alkalies could be removed by electrolysis, and by this method the dry ground powder gave a yield of 0.14 per cent. alkalies while as high as 0.45 per cent. were extracted from the wet re-ground material. From fourteen re-grindings and electrolytic runs on the same sample it was found possible to extract 3.54 per cent. alkalies with water alone, which represents a decomposition of about 27 per cent. and indicates that total decomposition could be brought about by repeating the operation of regrinding and electrolysis a sufficient number of times. Because of the time and energy involved in this method, the results obtained are, of course, interesting from a theoretical point of view only.

The action of water can, of course, take place only upon the free surfaces of the particles, and as this surface is a function of fineness of grain it was decided to attempt the determination of the relative amount of alkalies which could be extracted by water from samples of different degrees of fineness. For this purpose some of the feldspar was obtained in massive form, crushed in an iron crusher and then passed through a set of standard mesh sieves. The powder retained between each consecutive pair of sieves was given a number, and its particles assigned the average diameter of the two meshes. For the coarse material this method was considered sufficiently accurate. Material which would pass through the 200-mesh sieve was separated by the air elutriation into three samples and microscopic measurements were made as previously described.

The area of a unit weight, or in this case, a unit volume (1 cc.), of solid material broken down to the sizes represented by the different samples was then calculated, from the formula previously given, for use in comparing the relative amount of the alkalies liberated. The results of these measurements are given in the following tables:

TABLE I.—COARSE POWDERS.

No.	Mesh.	Average diameter. mm.	Area per cc. sq. cm.
1	10– 20	1.3970	43
2	20– 30	0.7239	83
3	30– 40	0.4695	128
4	40– 50	0.3465	173
5	50– 80	0.2493	241
6	80–100	0.1605	374
7	100–200	0.0994	604

TABLE II.—FINE POWDERS.

No.	Diameters. mm.	Per cent.	mm.	Per cent.	mm.	Per cent.	Area per cc. sq. cm.
8	0.0122	8	0.0061	15	0.00090	77	53,202
9	0.0063	3	0.0025	10	0.00018	87	292,685
10	0.0037	3	0.0007	14	0.00010	83	510,486

In order that a number of electrolyses could be carried on at the same time and under the same conditions, a battery of six cells was constructed as shown in Fig. 1.

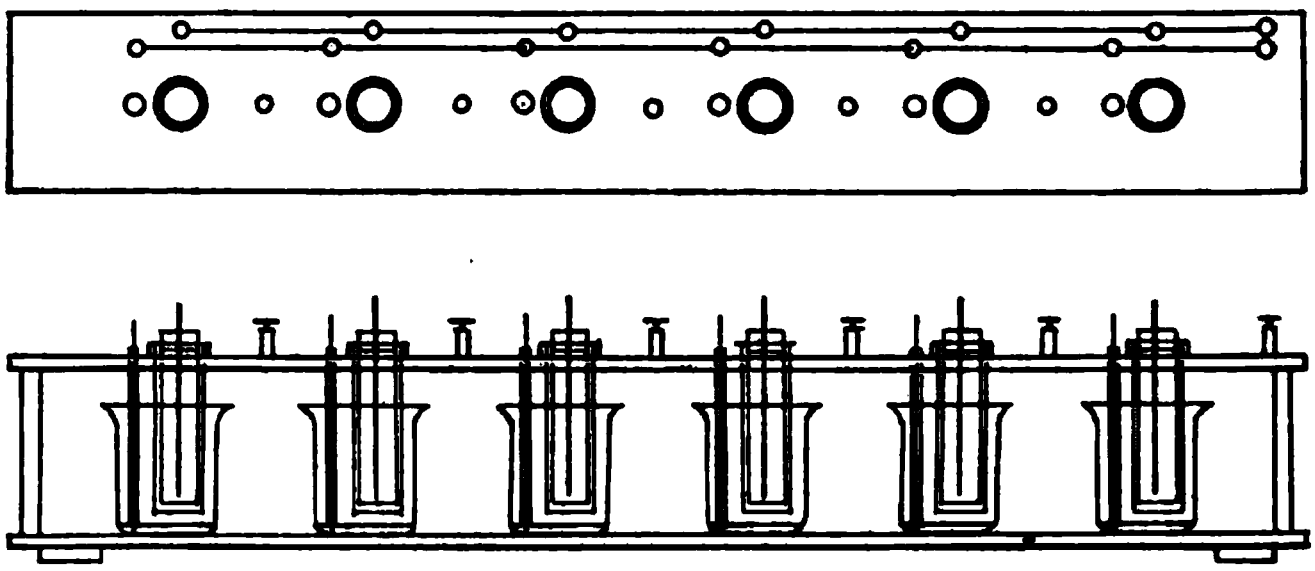


Fig. 1.—Arrangement of electrolytic cells.

Each of these cells consisted of a 400 cc. Jena glass beaker which served as cathode compartment and a cylindrical wooden pine cup 5 inches high—1.5 inches external diameter and 1/8 inch thick, for the anode or slime chamber, which also served as a porous diaphragm. An adjustable rubber collar placed around the tops of these cups allowed them to be hung in the rack above the beakers so that the bottom of each cup was about 0.5 inch from the bottom of the corresponding beaker. The anodes were made of heavy platinum wires which passed through stoppers fitted in the mouths of the wooden cups, and the cathode in each cell

consisted of a layer of mercury covering the bottom of the beaker and connected to the binding post by means of a platinum wire running through a sealed glass tube. The binding posts were arranged in such a manner that the cells could be connected either in parallel or series. When run in parallel the anode and cathode wires were connected to the binding posts joined to the main line while a series connection could be made by means of the auxiliary binding posts placed between the cells in such a manner that the cathode of one could be connected to the anode of the next. The cups were first treated with alcohol to remove as much resin as possible and then well soaked in water. Blank runs were made upon each cup until no indication of alkalinity could be observed by the use of phenolphthalein in the cathode compartment.

Twenty grams each of the coarse samples were slimed in the anode chamber with 50 cc. distilled water and 200 cc. distilled water was placed in the cathode compartment. The cells were run in series on a 220-volt line. A number of 48-hour runs were carried on until practically no more alkalies were liberated, and titrations of the cathode liquor with N/10 HNO_3 made at the end of each run to determine the amount of $K_2O + Na_2O$ extracted. Each run was begun with fresh distilled water in the cathode compartment. Electrolyses of the fine powders were

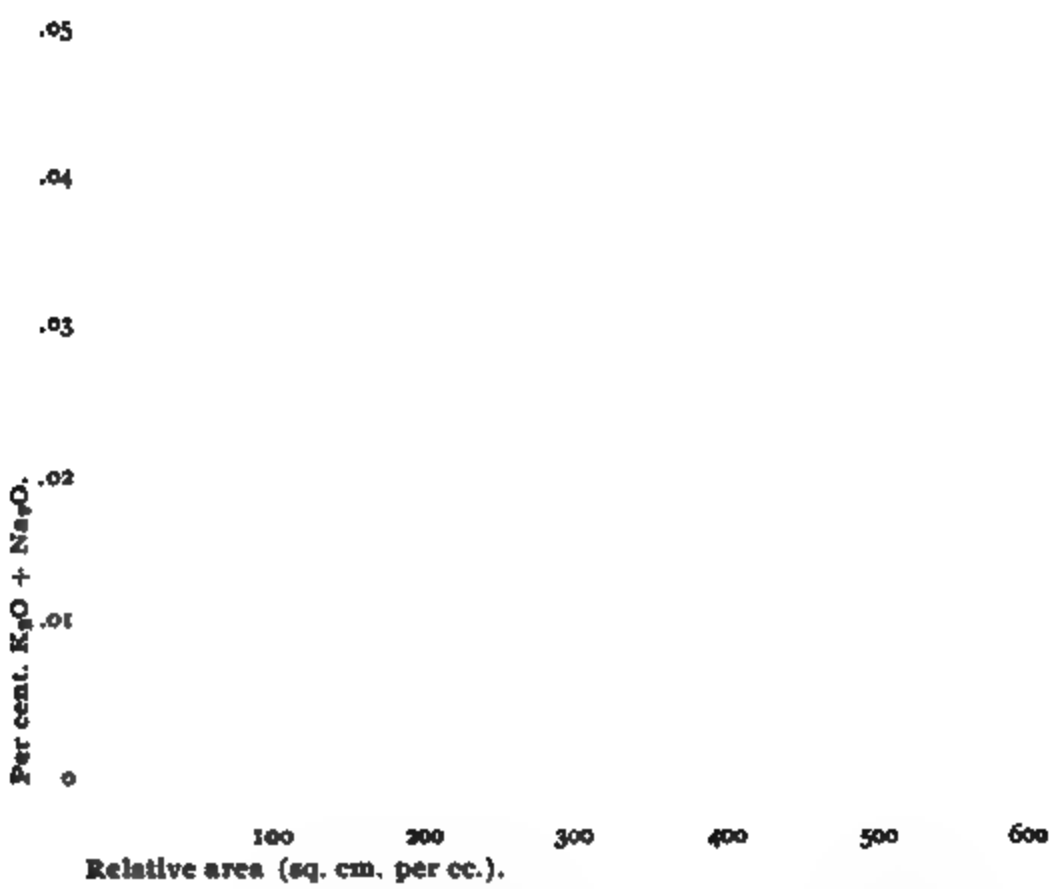


Fig. 2.—Electrolysis of orthoclase with water (coarse powders).

made in the same manner with the exception that, the supply being somewhat limited, 3 grams were used instead of 20. The results for both the coarse and fine powders are given below and are followed by diagrams (Figs. 2 and 3). It was found necessary to construct diagrams

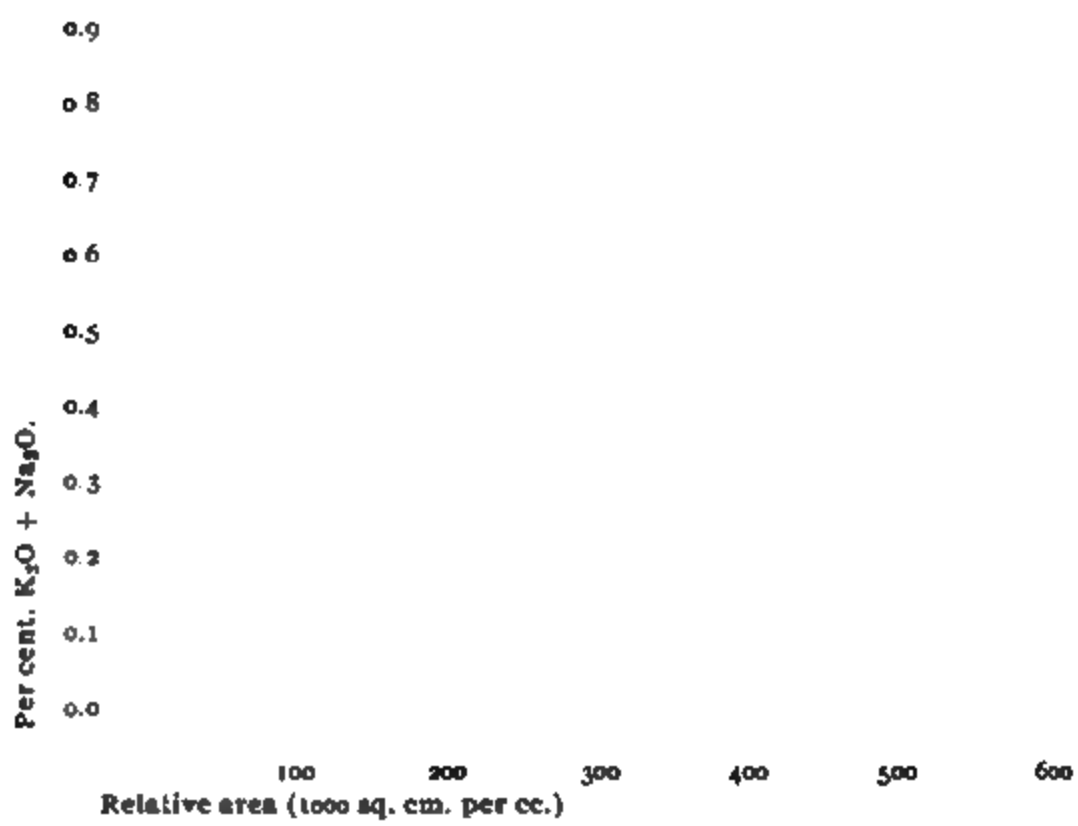


Fig. 3.—Electrolysis of orthoclase with water (fine powders).

of different scale for the coarse and fine powders, as the relative areas exposed make it impossible to compare the different order of magnitudes on one scale.

TABLE III.—COARSE POWDERS.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.
Sq. cm. per cc ...	43	83	128	173	241	374	604
Per cent. $K_2O + Na_2O$	0.013	0.017	0.021	0.026	0.027	0.029	0.054

TABLE IV.—FINE POWDERS.

	No. 8.	No. 9.	No. 10.
Sq. cm. per cc.....	53,202	292,685	510,486
Per cent. $K_2O + Na_2O$.....	0.423	0.683	0.873

Although these results plainly show an increased yield, the solution effect is not in exact ratio to the increase of surface area. It is probably true that as the particles decrease in size the tendency to clump and coagulate increases, and that, therefore, the theoretical surface area obtained does not entirely come into play. Although our investigations do not include a sufficient number of different sized powders to demonstrate this point, it is apparent, from theoretical considerations, that

some reverse action must take place with increasing fineness. If this were not true, powdered orthoclase made up of ultimately fine particles should be rapidly and completely decomposed by water, which is not the case. This point will be discussed more fully later on, but it may be stated that this case is not essentially dissimilar to that of the gas law, which is subject to an increasing correction with increasing pressure until finally it no longer holds. It is not to be supposed that the decomposition of the feldspar is actually effected by the action of electrolysis, as the electric current merely transfers the soluble basic products of the hydrolysis. The simplest reaction which can be written to express the action of water on orthoclase is as follows:

$$KAlSi_3O_8 + HOH = HAlSi_3O_8 + KOH.$$

By a splitting off of silica from the hydrated aluminum silicate we can account for the formation of kaolin.

$$2HAlSi_3O_8 + H_2O = (H_2O)_2.Al_2O_3.(SiO_2)_2 + 4SiO_2.$$

It is certain, however, that the actual reactions which take place during the process of kaolinization in nature are more complex than these, and that intermediate zeolitic compounds of varying composition are formed in which water, if not potash itself, is held in the form of a solid solution.[1] It is difficult to determine whether similar intermediate products are formed when water acts on orthoclase powder under the conditions maintained in these experiments. It has been shown, however, that in whatever condition the potash is held in the decomposition products of orthoclase it is possible to extract it by electrolysis.

As feldspar is known to be partially decomposed by concentrated sulphuric acid, it was thought that a comparison of the decomposition of different sized powders could be readily obtained by this means. A series of digestions and determinations of alumina was accordingly made, and while the time exposed and relative proportions of powder and acid varied somewhat in the different experiments, as described under the respective tables, the method in general was as follows:

Weighed amounts of the powder were mixed with known volumes of H_2SO_4 (sp. gr. 1.84) and allowed to digest on the steam-bath for definite lengths of time. They were then diluted and filtered, and either the whole or an aliquot part of the clear filtrate was analyzed for alumina in the usual manner, by precipitation with NH_4OH. If the filtrate was cloudy, a sufficient amount of ammonia was added to cause the suspended particles to settle, but not enough to neutralize the acid and precipitate the alumina. An aliquot portion of the clear supernatant liquid was then analyzed.

The coarse powders were obtained in the same manner as described for the electrolysis, with H_2O, with the addition of thoroughly washing

[1] *Z. anorg. Chem.*, 15, 318.

them on the sieves with a strong stream of water after they had been dry-sifted. They were then dried and all traces of iron from the crusher removed by means of an electro-magnet. Six grams of each sample were digested with 10 cc. of acid for eighteen hours, as described. Fig. 4 and its accompanying table give the results of these experiments.

TABLE V.—COARSE POWDERS.

Sq. cm. per cc.	43.	83.	241	604.
Per cent. Al_2O_3	0.041	0.078	0.098	0.160

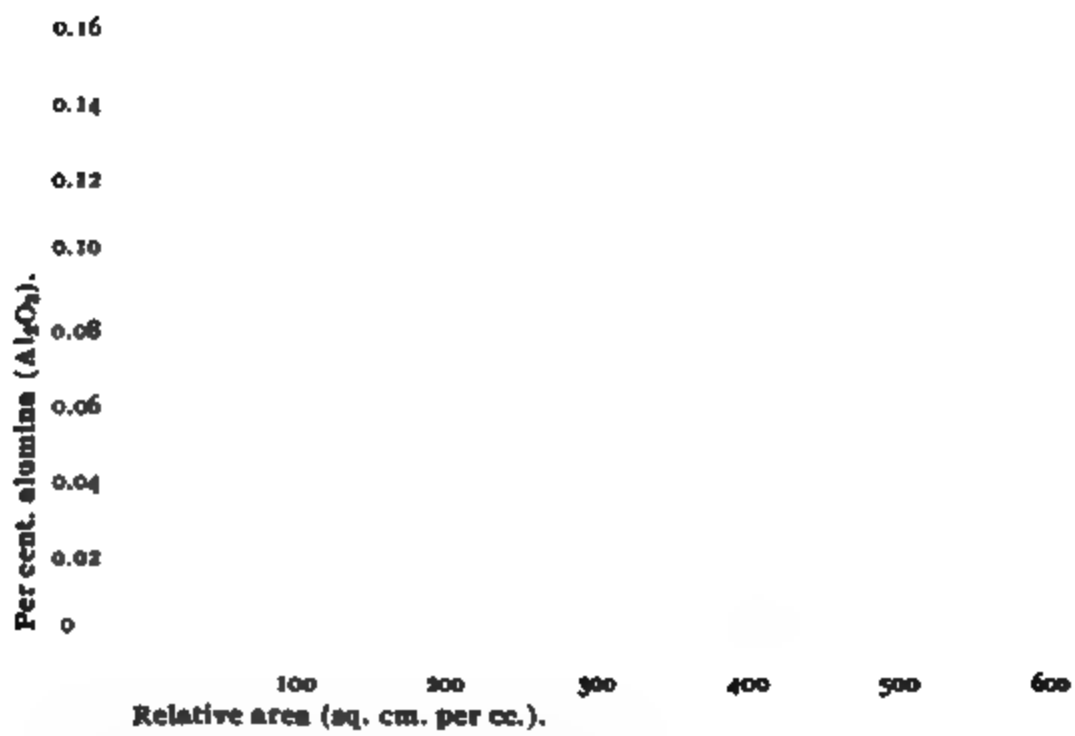


Fig. 4.—Solubility of orthoclase in sulphuric acid (coarse powders).

Four different experiments were made upon the air elutriated powders, the conditions and the results being given in the following table, made to accompany Fig. 5. Microscopic measurements and determinations of relative volume proportions were made in the same manner as described for the fine material in the electrolytic experiments. As the surface areas were also calculated in the same manner, it seems unnecessary to give the actual measurements here.

TABLE VI.

Symbol.	Conditions.		Chamber. 1.	Chamber. 2.	Chamber. 3.	Chamber. 4.	Chamber 5.
●	3 gms., 24 hrs.	Per cent. Al_2O_3	0.333	0.747	....	....	2 007
	10 cc. H_2SO_4	sq. cm. per cc.	5,958	11,184	....	....	526,080
△	6 gms., 18 hrs.	Per cent Al_2O_3	0.267	0.480	....	1.107	.
	10 cc. H_2SO_4	sq cm. per cc.	5,958	11,184	....	95,160	.
⊡	6 gms., 96 hrs.	Per cent Al_2O_3	0.313	0.643	1.090	....	.
	10 cc. H_2SO_4	sq. cm. per cc.	5,958	11,184	34,284	....	.
X	6 gms., 19 hrs	Per cent. Al_2O_3	0.187	0.357	0.587	0 750	1 010
	10 cc H_2SO_4	sq. cm. per cc.	5,118	9,546	21,366	103,470	475,314

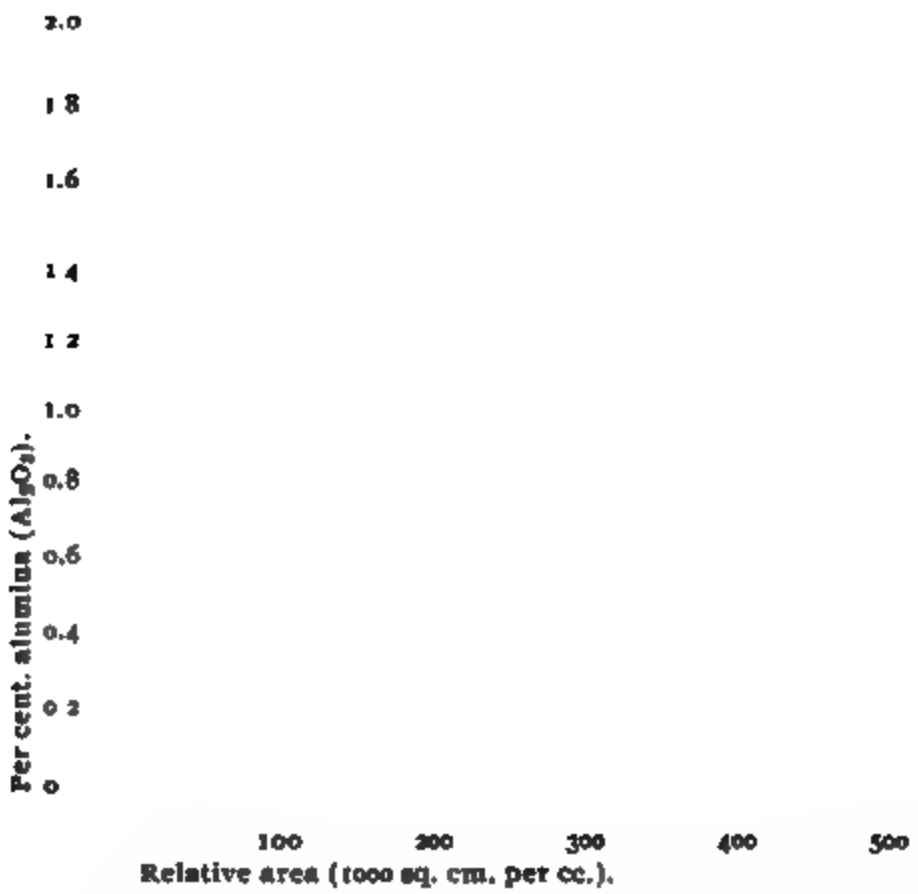


Fig. 5.—Solubility of orthoclase in sulphuric acid (fine powders).

In reviewing the diagrams for solubility with respect to area exposed, it will be seen that there is unquestionably a tendency toward greater solubility as the powder becomes finer, but here again in no case is the solubility shown to be directly proportional to the surface area. As these differences are in every case too great to be laid to the charge of experimental error in analysis, it was decided that it would be of interest to determine the solubility of some substance about which there could be no question in regard to surface area exposed to the action of a solvent. Sheet copper was selected as being the most homogeneous material readily obtainable, and pieces of known area, after being thoroughly cleaned, were subjected to the action of normal nitric acid for the same length of time in the same vessel, especial precautions being taken to keep the temperature as constant as possible and thus to avoid convection currents. The loss in weight of the samples was then determined and the results plotted as shown in Fig. 6.

A number of tests were made, in which the size of the test pieces and the concentrations of acid were varied, but in every case the curve representing any one series was more or less erratic in its direction.

It is certain that varying conditions play an important part in the relative solubility of different sized particles of the same material, but within certain limits the solubility or decomposition effect rises rapidly with increasing fineness.

In previous work it was demonstrated that when powdered feldspar was slimed with water and a small amount of hydrofluoric acid and electrolyzed in the manner described for the water electrolyses, a far greater amount of decomposition took place than could be theoretically deduced from the action of the quantity of hydrofluoric acid present.[1] This result was due to the regeneration of the acid and in the run described it was found that 87 per cent. decomposition had been produced by the action of 20 cc. of 35 per cent. hydrofluoric acid upon 200 grams of the ground orthoclase. All of the bases, including alumina, were carried to the cathode compartment, the alumina being held mainly in solution as an alkaline aluminate, while silica alone is the final product left at the anode.

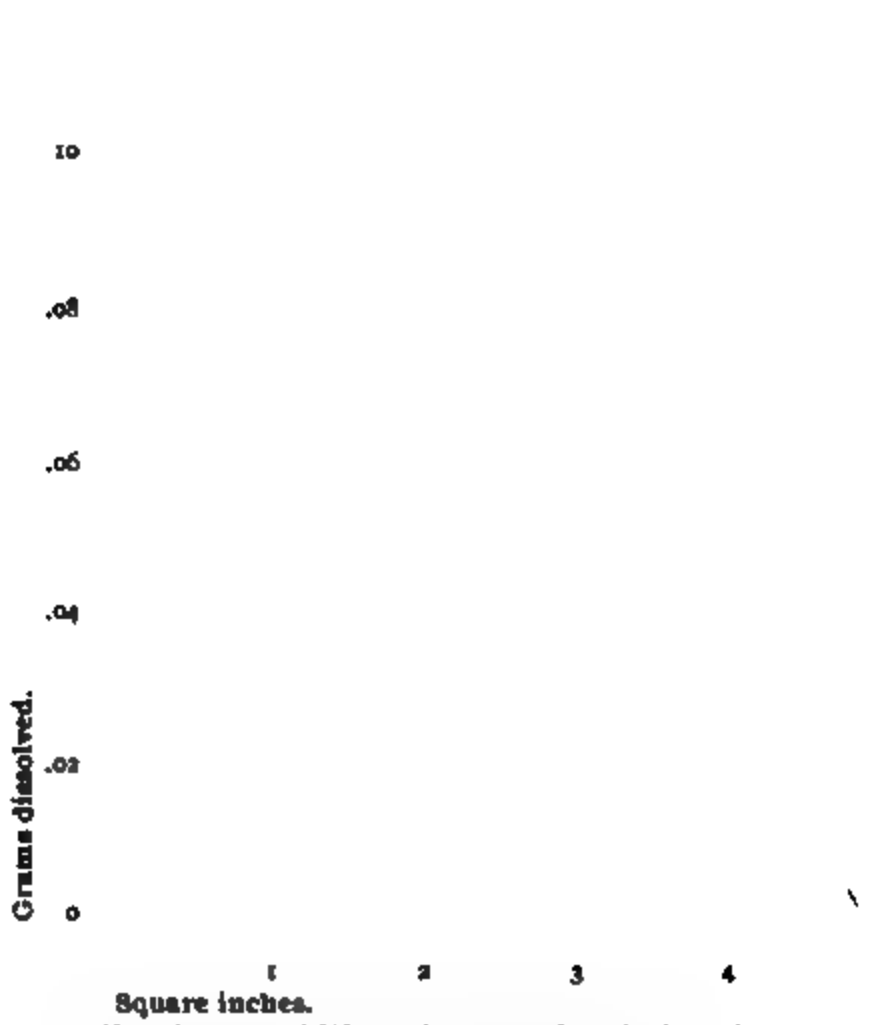


Fig. 6.—Solubility of copper in nitric acid.

The mechanism of these reactions would seem to be as follows: Taking, for the sake of convenience, an abbreviated form of the orthoclase molecule and considering the primary reaction when attacked by hydrofluoric acid, we may write the following equations:

$$1.\ 4KAlSi_3O_8 + 64HF = 4KF + 4AlF_3 + 12SiF_4 + 32H_2O.$$

If potassium fluoride is added to a solution of aluminum fluoride, a difficultly soluble double salt is formed, and so we should expect the following reaction:[2]

[1] *Bull. 28, Office Public Road., U. S. Dept. Agr.*

[2] Dammer's Anorg. Chem., III, 97.

$$2.\ AlF_3 + 4KF = AlF_3.4KF.$$

This slightly soluble double salt is slowly hydrolyzed, the potash and alumina being carried to the cathode chamber while the hydrofluoric acid is set free at the anode to immediately attack fresh orthoclase particles.

The silicon tetrafluoride is changed to hydrofluosilicic acid and silicic acid according to:

$$3.\ 12SiF_4 + 16H_2O = 4Si(OH)_4 + 8H_2SiF_6.$$

Finally it appears that the hydrofluosilicic acid is again broken up by hydrolysis according to:

$$4.\ H_2SiF_6 + 4H_2O = 6HF + Si(OH)_4.$$

It has been shown that only about one-tenth of the amount of hydrofluoric acid necessary to complete the reaction, according to the stoichiometrical relations involved, suffices to bring about complete decomposition of the orthoclase. This can only be explained by supposing that some such reactions as are given above take place.

The next problem was to study the effect of fineness of grinding on the rate of decomposition. No relation between the amount of decomposition with respect to area exposed can be determined unless the reaction proceeds to a finish and as, in the electrolysis of orthoclase with hydrofluoric acid, this point is reached only when decomposition is complete, it is evident that a comparison between these two factors is impossible by this means. The effect of fineness upon the time necessary for complete decomposition under the same conditions can, however, be determined, and with this object in view electrolyses with hydrofluoric acid were made on the three fine powders described as Nos. 8, 9 and 10 in the water electrolyses. One cubic centimeter of hydrofluoric acid was added to each of the anode liquors and the runs continued as before, with the exception that the cells were connected in parallel instead of in series. The length of these runs was the same for all of the cells in each particular case, but the amount of current flowing varied somewhat, of course, with the individual cells. In the sixth run another cubic centimeter of acid was added in order to hasten the operation. The cathode liquors were carefully titrated with standard acid after each run, and the results obtained are given in the following table:

TABLE VII.

	Run.	Time. Hours.	No. 8. cc.	No. 9. cc.	No. 10. cc.
	With water alone.....		2.70	4.35	5.55
1	with H F.....	48	6.45	8.55	13.65
2	" "	24	8.55	9.65	11.20
3	" "	24	7.70	9.00	11.15
4	" "	24	5.00	5.35	7.35
5	" "	24	0.30	2.20	2.80

TABLE VII (*Continued*).

			Time. Hours.	No. 8. cc.	No. 9. cc.	No. 10. cc.
6	Run. "	"	24	5.40	10.80	18.20
7	"	"	24	2.00	6.40	6.15
8	"	"	24	2.20	8.95	6.10
9	"	"	24	5.45	11.25	1.95
10	"	"	48	9.65	5.20	0.15
11	"	"	24	8.85	0.50	0.00
12	"	"	24	8.70	0.30	
13	"	"	24	5.15	0.00	
14	"	"	24	2.70		
15	"	"	24	2.40		
16	"	"	24	1.50		
17	"	"	24	0.10		
18	"	"	24	0.00		
Total cc.				84.80	82.50	84.25
No. of hours				456	336	288

It will be noticed that the reaction was completed with the finest powder first, the next finest second, and the coarsest third.

The actual amounts of alkalies set free as shown by the total titrations are given in the following table. In order to calculate the per cent. decomposition which this represents, it was found necessary to determine the quantity of alkalies present in the three classes of material obtained from the air elutriator, as the relative amount of quartz present in the samples varied with the different sizes, owing to its greater hardness and consequent lack of fineness. All of these results are given below:

TABLE VIII.

	No. 8.	No. 9.	No. 10.
Alkalies liberated from 3 gms.	0.3998 gm.	0.3890 gm.	0.3972 gm.
Per cent. alkalies liberated	13.33%	12.97%	13.24%
Per cent. alkalies contained	13.29%	13.63%	13.74%
Calculated per cent. decomposition	100.00%	95.16%	96.36%

To check this work very roughly, an analysis was made of the residue obtained from the electrolysis of sample No. 3. It was found to contain silica and alumina in the following proportions:

	Per cent.
SiO_2	98.80
Al_2O_3+	1.13
Total	99.93

It would seem, therefore, that all of the alkalies had been liberated instead of 96.36 per cent., as represented in the preceding table. The low results obtained on samples 9 and 10 by titration are undoubtedly due to a slight diffusion of the hydrofluoric acid through the wooden

cups to the cathode compartment. The reason for the fact that some alumina was present in the residue is explained by the low solution pressure of aluminum fluoride, which allowed the more soluble alkaline fluorides to be transported first. It was noticed that as the yield of alkalies decreased alumina came over in greater amounts, and this transfer would have undoubtedly been complete had electrolysis been carried further.

Assuming, therefore, that decomposition in each of the three cases was complete, the approximate effect of surface area upon time necessary to bring about this decomposition can be shown as in Fig. 7, when the ordinates represent the time covered by the total number of runs and the abscissas the surface area presented.

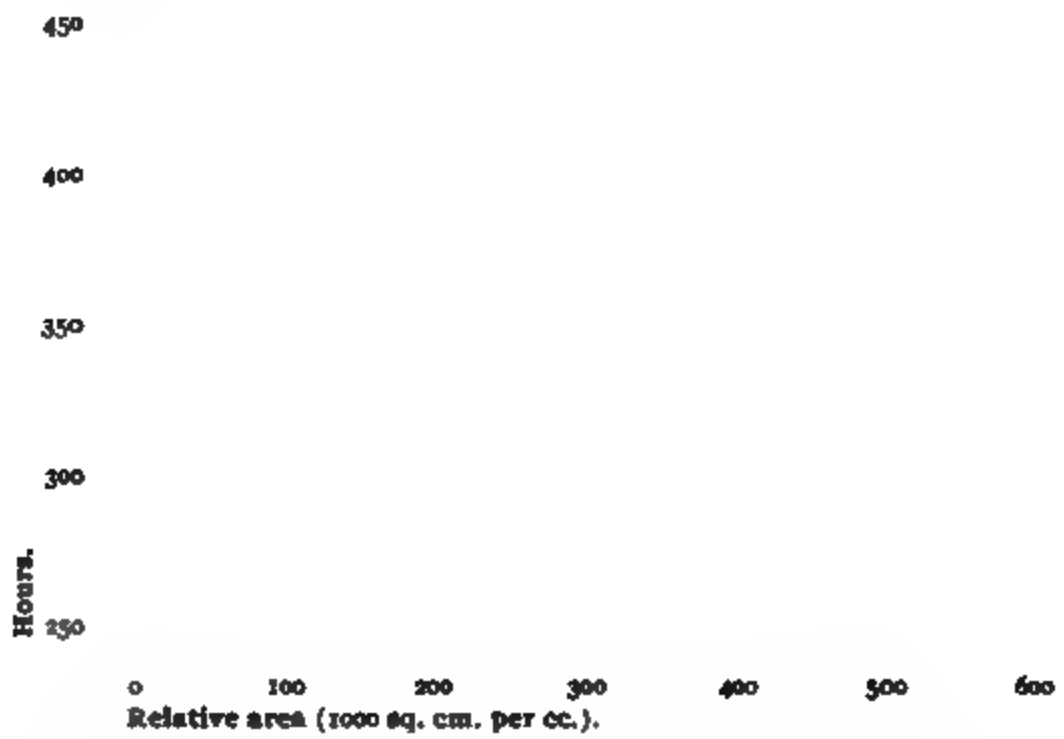


Fig. 7.—Electrolysis of orthoclase with hydrofluoric acid (fine powders).

In reviewing the diagrams showing the effect of fineness upon the extent of decomposition with water, as well as upon the time required to bring about complete decomposition with hydrofluoric acid, it will be noted that while the results do not strictly conform to theory, important differences in the reacting power of the different sized powders are shown to exist. The same remarks which were made upon the experiments with sulphuric acid are applicable here, and while it is true that a number of factors which it is impossible to take into account have a very important bearing upon work of this nature, it is nevertheless evident that in the extraction of potash from feldspathic rocks or, in fact, in any process of a similar nature, the effect of surface area of fineness of the material is a factor which deserves serious consideration. The slight solubility of the double fluorides of aluminum and potassium is one cause of the slowness of the separation of the bases in the electrolytic process,

but it is possible that this difficulty might be overcome if the work were being conducted upon a large scale. Even if these difficulties did not exist, however, the prevailing price of potash and high cost of electrical energy would probably be a bar to the electrolytic process.

A study of the decomposition of the feldspars could not be considered complete unless it included all the methods of attack which have been proposed by others, or which have suggested themselves to the writers. The analytical method of J. Lawrence Smith, for decomposing silicates, has very naturally been made the basis of a number of processes, on some of which patents have been granted in various countries. Patents for fusion methods with salt or lime, or both, in combination, were granted in England to Tilghman 1847, Newton 1856, and Ward 1857.[1] In 1882 Spiller proposed a method for making potash alum from feldspars, which depended upon treating a mixture of the ground minerals with sulphuric acid. Pemberton showed later that this method could not possibly produce alum for a sufficiently low cost to justify its use.[2] More recently, Rhodin's process of fritting at 900°, a mixture of 100 parts of ground feldspar with 53 parts of quicklime and 40 parts of salt, has been to some extent exploited in England and in Sweden.[3] By this process it is claimed that about 90 per cent. of the potash present is converted into chloride and can be easily leached from the frit. It is possible that this mixture could be burned in continuous rotary kilns operated in a similar manner to those in use in cement manufacture. The fact, however, that the salt and lime combine with the silica and alumina to make a by-product of little or no value has undoubtedly prevented the development of this method into a commercial process. Lake has lately obtained an English patent[4] for treating leucite with sodium hydroxide or carbonate and quicklime. The inventor writes the following reactions in describing his process:

1. $Al_2O_3.K_2O.4SiO_2 + 4NaOH + 3CaO =$
$$Na_2O.3CaO.4SiO_2 + Al_2O_3.Na_2O + K_2O + 2H_2O:$$
2. $Al_2O_3.K_2O.4SiO_2 + 2Na_2CO_3 + 3Ca(OH)_2 =$
$$Na_2O.3CaO.4SiO_2 + Al_2O_3.Na_2O + K_2O + 2CO_2 + 3H_2O.$$

Although complete decomposition undoubtedly takes place by this method, the above reactions are open to criticism. There is no apparent reason why the soda should all enter into combination, leaving potash in a free state. Blackmore[5] has been granted a patent for the separation of alkali salts from insoluble combinations by treat-

[1] *J. Soc. Chem. Ind.*, 20, 5, 440.
[2] *Chem. News*, 47, 1206, 5.
[3] *J. Soc. Chem. Ind.*, 20, 5, 438.
[4] *English Pat.*, 17,985.
[5] *U. S. Patent*, 772,206 (1904).

ment with carbonic acid under high pressure. The writers have had no experience with this method, but it is doubtful whether, even if it is successful chemically, it could be developed into a commercial process.

The writers have found that fusion or fritting with calcium chloride will decompose feldspar but here again, even under the most favorable circumstances, it is unlikely that such a method of attack could be made economical.

Sodium nitrate and mixtures of sodium carbonate and nitrate decompose feldspars at comparatively low temperature. As sodium nitrate is extensively used as a fertilizer, and as it may possibly be eventually manufactured in part from atmospheric nitrogen, it is at least interesting to note in passing that it is possible to enrich it with soluble potash by fusion with ground feldspar and regrinding.

It will be seen, however, that the weak point in all the methods of attack so far discussed is the unavoidable formation of large quantities of by-products which, though made from more or less costly raw materials, are of no value in the end. This difficulty can apparently only be overcome by the use of potash compounds to attack the feldspar, since the potash used is at least as valuable after the process is completed as it was before. The writers have tried a number of methods of attack with various compounds of potash. Some of these experiments have led to interesting results which may possibly be found to have a bearing upon the practical problems of potash extraction. If fine-ground orthoclase is mixed with potassium carbonate or hydroxide and heated at a dull red heat for a short time, the decomposition of the feldspar takes place rapidly. The decomposition becomes complete when the orthoclase and potassium carbonate are present in the ratio of 1 : 1.6 parts. On taking up with hot water a white flocculent precipitate of definite composition is formed which is readily soluble in dilute acid. On careful analysis of this white precipitate, made from different samples of orthoclase, it appears to be the potassium analogue of natrolite, the well-known sodium aluminum orthosilicate, the formula of which is

$$(H_2O)_2K_2OAl_2O_3(SiO_2)_3.$$

Fusions were made of two different orthoclases in the following manner:

One-half gram of the powdered orthoclase was ground with 0.8 gram of potassium carbonate, the mixture transferred to a platinum crucible and heated to a dull red for 15 minutes. When cool, the fusion was taken up with hot water, digested on a steam-bath for five minutes in order to obtain a flocculent precipitate, and filtered, the precipitate being washed with boiling water until the last washings were neutral to litmus. The precipitate or synthetic silicate was then dissolved in hydrochloric acid and analyzed in the ordinary manner. The following table gives the results obtained, calculated in per cent. of the original powder taken:

TABLE IX.

	Theoretical orthoclase.	Orthoclase. A.	Synthetic silicate from A. 1.	Synthetic silicate from A. 2.	Orthoclase. B.	Synthetic silicate from B. 1.	Synthetic silicate from B. 2.
SiO_2	64.84	68.29	33.68	33.80	66.52	32.78	32.78
Al_2O_3	18.29	18.27	18.36	18.24	18.32	18.32	18.26
P_2O_5	...	0.53	0.15	0.16	...	...	...
K_2O	16.87	9.32	16.28	16.39	13.53	17.54	17.36
Na_2O	...	3.60	1.19	1.16	1.63	...	...
	100.00	100.01	69.66	69.75	100.00	68.64	68.40

Using the data given above, the percentage composition of these precipitates can be calculated, showing the probable synthesis of a potash analogue of natrolite. The percentage composition of an anhydrous potash form of natrolite is also given for the sake of comparison.

	Composition of anhydrous potash form of natrolite.	Composition of anhydrous residue from orthoclase A.	Composition of anhydrous residue from orthoclase B.
SiO_2	47.97	48.51	47.84
Al_2O_3	27.06	26.32	26.69
K_2O	24.97	25.17	25.47
	100.00	100.00	100.00

The above results can best be interpreted by the following reactions:

1. Reaction during fusion.

$$K_2O.Al_2O_3(SiO_2)_6 + 6K_2CO_3 = 6K_2SiO_3 + K_2Al_2O_4 + 6CO_2.$$

2. Reaction of fusion with water:

$$6K_2SiO_3 + K_2Al_2O_4 + 5H_2O = (H_2O)_2.K_2O.Al_2O_3(SiO_2)_3 + 6KOH + 3K_2SiO_3.$$

Leaving aside the question of whether or not such a method of attack could be considered from a commercial standpoint, it is none the less apparent that complete decomposition of the feldspar takes place, with a synthesis of a silicate rich in potash which would be easily made available in the soil or for further extraction treatment in the factory.

The latest process for the extraction of potash from feldspar which has been granted a patent in the United States is that of Swayze,[1] which takes advantage of the principle of the potash attack upon the silicate. According to the specifications for this process, coarsely ground feldspar is first heated to partially destroy its crystalline structure, and it is then heated under pressure with a strong solution of caustic potash. By subsequent chemical treatment it is proposed to manufacture potash, alum and fine silica as the end products of the various operations. Although it is doubtless true that orthoclase can be largely decomposed by this method, the reactions involved are necessarily similar to the fusion methods just described with subsequent treatment with water, and it is doubt-

[1] *U. S. Patent*, 862,676 (1907).

ful whether the necessary separations of the products could be profitably made.

Another method which has suggested itself, as a result of the writers' investigations, is treatment of the ground orthoclase with a certain proportion of hydrofluoric acid, taking advantage of the reactions given on pages 790–1, but without the subsequent electrolysis. By filtering cold on a cloth filter, nearly all of the potash present is held in the residue in the form of a double fluoride with alumina. By subsequent heating with ground limestone or lime, the potash is readily made soluble, and, if it is desired, can be leached out. Unfortunately, the excess of lime present makes it impossible to recover the hydrofluoric acid.

It would seem probable that some one of these methods which have been described or suggested, could be developed under favorable circumstances into a successful commercial process. The above data are presented in the hope that it will stimulate experimentation on a larger scale than is possible in a chemical laboratory and result in a successful solution of an important industrial problem.

The results given in this paper may be summarized as follows:

(1) Fine grinding of feldspars renders the potash partly available under the action of water. The addition of certain substances, such as ammonium salts, lime and gypsum, increases this effect.

(2) It is possible to completely extract potash by an electrolytic method either with or without the addition of hydrofluoric acid, but it is probable that this method could not be used commercially on account of its cost.

(3) The effect of fineness of grinding has been studied and data given showing the relation of surface area to rate of decomposition.

(4) It is shown that there are numerous fusion methods which could be used successfully if the cost were not too high. The attack on the silicates by means of potash or its compounds yields some interesting reaction products which might possibly be made use of.

(5) The attack with hydrofluoric acid is suggested as a possible method that deserves further study.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

FLASK FOR FAT DETERMINATION.

W. L. DUBOIS.

Received February 21, 1908.

The Knorr apparatus for the extraction of fat employs a flask which is fragile, very difficult to clean and expensive to replace. A number of attempts have been made to supplant these flasks with simpler ones

more easily cleaned, and the breakage of which would not be such an important matter.

The first flask designed to meet this requirement is that described by Wheeler and Hartwell.[1] In this apparatus the designers have used a straight-necked flask holding about 100 cc., fitted with a rubber cup channeled so as to receive the condenser. Some workers, however, have found this device somewhat unsatisfactory, owing to the short life of the rubber cups and some danger attending their use. The modification of this idea, shown in Fig. 1, was designed by Mr. F. W. Robison, of the Michigan Dairy and Food Department. As is indicated in Fig. 2, the seal consists of a maple cup made to fit over an ordinary rubber stopper through which the neck of the flask is passed. The seal is made by mercury in a manner similar to the device employed by Wheeler and Hartwell. This form of apparatus is now used in one of the laboratories of the Department of Agriculture and is considered a great improvement over the Knorr flask.

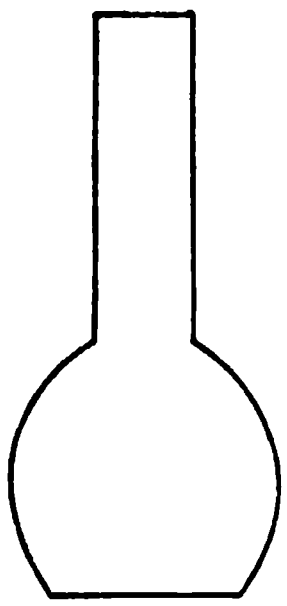


Fig. 1.

The flask designed by the writer and shown with connections, in Fig. 2, is a modification of the above. Being of the Erlenmeyer type, cleaning is more easily accomplished, while at the same time all the good features of the above-described flasks are retained. The one used in this laboratory holds about 100 cc. and weighs approximately 30 grams, this tare affording considerable strength while not affecting the accuracy in weighing. In practical use the flask is proving about all that could be desired in regard to safety and ease of manipulation, facility in cleaning and small expense for replacement.

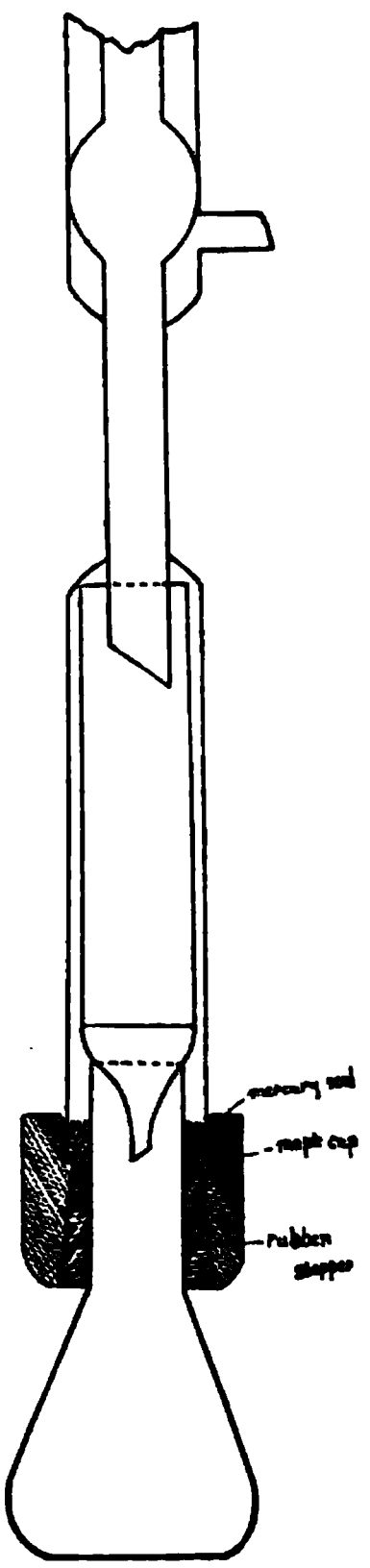


Fig. 2.

BUFFALO LABORATORY.

A PROPOSED METHOD FOR THE ROUTINE VALUATION OF DIASTASE PREPARATIONS.

BY WILLIAM A. JOHNSON.

Received February 21, 1908.

In view of the rapidly increasing number of starch-digesting products on the market, and the exaggerated claims which are made for some of

[1] THIS JOURNAL, 23, 338.

them in the literature, through which they are advertised to physicians and others interested, the necessity for a simple and approximately accurate method of valuation becomes every day more apparent. This necessity would not be so urgent if the manufacturers of these amylolytic ferments had agreed among themselves on a uniform method by which the enzymic activity may be determined, but this they have not done and apparently are not likely to do.

In the last two years committees of the Council on Pharmacy and Chemistry of the American Medical Association have undertaken to pass on the validity of the claims of the manufacturers of medicinal substances for the strength and purity of their products, among which products the diastatic mixtures occupy an important place. In the course of some investigations on the subject, which I have carried out under the direction of one of these committees, I have made a number of observations which have a bearing on the question of the value of the methods and these I now wish to put on record.

It may be said at the outset that nothing fundamentally new will be offered here. Indeed this is not necessary in view of the classic researches of Brown and Morris, Brown and Heron, O'Sullivan, Roberts, Kjeldahl, Lintner, Effront and others, to say nothing of the older studies of Dubrunfaut, Payen and Musculus.[1]

But most of the methods of measuring the ferment activity as brought out in these long studies had for their main object the valuation of malt employed in the brewing industries, and because of this fact they are not usually available for the work we have in hand. In general, such valuation may be made by noting the amount of the diastase preparation required to completely discharge the color of the iodine reaction in a given weight of starch paste of definite strength, or by noting the amount of sugar formed from an excess of starch, by the enzymes in some definite time at a proper temperature. From a theoretical standpoint, methods based on the latter determination would seem to have the advantage, as sugar formation rather than starch disappearance is the end practically required. But in some classes of preparations the enzyme is mixed with so large a quantity of glucose or maltose that the determination of more sugar formed would be found difficult in practice, especially where the ferment activity is low. This objection does not obtain in the observation on the disappearance of the starch-iodine reaction.

It is true that this starch-iodine method has been frequently condemned

[1] The general literature on the subject of the digestion of starch is of course voluminous, and no attempt will be made to quote all of it. But reference may be made to the convenient résumés in the following works: v. Lippmann, "Chemie der Zuckerarten," III Edition. Oppenheim, "Die Fermente und ihre Wirkungen." Effront, "Die Diastasen."

because the end point indicated by the disappearance of the iodine reaction is a point measuring the formation of a mixture, possibly, of somewhat complex dextrins with sugar, rather than of maltose itself. But if it may be shown that the disappearance of the iodine reaction follows always when a rather constant amount of maltose is formed, the method may be made of value for practical purposes. The correspondence between sugar formation and starch disappearance obtains, however, only under definite conditions, the redetermination of which was the first object of my experiments.

Roberts was the first, apparently,[1] to work out a method for the comparison of diastatic activities through the aid of the iodine-starch reaction. This general method was first used by F. C. Junck[2] and later by J. M. Francis,[3] who supplied many working details, which contribute much to the general accuracy and convenience of the process. In the accurate comparison of diastases in this way the essential points to be observed are these: 1. A pure standard starch must be made and this must be used in the form of a thin paste of constant value. 2. The experiments must be so conducted as to show a sharp end reaction between the iodine and vanishing starch. 3. A standard time limit must be adopted and rigorously adhered to. 4. The reaction must be carried out at a constant temperature.

In my experiments, in agreement with many others who have investigated the subject, I have found potato starch the best material to use as a standard. Most of the corn starch on the market seems to be wholly unfit for the purpose; in fact, different samples tested have given often final results varying by 50 per cent. or more from each other. But potato starch comes from the market in nearly pure form and by a simple treatment may be made suitable for use. For my experiments I washed 500 grams repeatedly with distilled water, by decantation, then sucked as dry as possible on a Buchner funnel. The mass was then spread on glass plates and dried 3 hours in an air current at a temperature of 50°. This made it dry enough to rub in a mortar, after which it was dried at 80° through four hours, which brought the moisture content down to 9.5 per cent., when the product was rubbed up again and bottled. It is not advisable to try to dry beyond 90 per cent. of pure starch, as the anhydrous starch absorbs moisture so quickly as to introduce inaccuracies in weighing. Prepared in this way, the microscopic examination shows clean granules, free from fracture and free from foreign substances.

It is hardly necessary to insist that a colorless end point is much more accurately and easily observed than is the point where the blue starch-

[1] *Proc. Roy. Soc.*, 32, 145. Cit. Maly's "Jahresber." for 1881, p. 290.

[2] *Am. Jour. Pharm.*, June, 1883.

[3] *Bulletin of Pharmacy*, February, 1898.

iodine reaction gives place to the reddish starch-dextrin reaction. I have worked then, in every case, to the colorless end point. With a little practice this may be uniformly noted by different observers working with the same materials, yet many persons have failed to realize the importance of this, as will be shown below.

On the question of the time limit in the digestions, there is greater room for difference of opinion, and various intervals from five minutes to one hour have been suggested by different workers. As the rapidity of starch conversion is very accurately proportional to the amount of enzyme present, it is in any case possible to reduce the time required to secure the desired end reaction by starting with a larger weight of the ferment, and the time finally selected as the standard or limit must depend, therefore, on a practical acquaintance with a wide range of substances in which such tests are made. In carrying out a number of tests in parallel, as is always the custom in such work, five minutes is an inconveniently short time to complete the various manipulations necessary; on the other hand, an hour, or even half an hour, is a relatively long time, which must be considered in part wasted if the same degree of accuracy can be secured in a shorter period. Now, it has been found, as a matter of fact, that no one of the digestive ferments on the market is so strong as to convert over 300 times its weight of starch into reducing sugar in ten minutes, while many of them have between one-tenth and one one-hundredth of this activity. Suppose, therefore, that we start with 1 g. of starch, the weights of enzyme preparation necessary to effect conversion in this time would run from 3.33 up to 33.3 or 333 mgs., quantities which are reached by convenient dilutions. Ten minutes seem to afford ample time to make the final color tests and I have therefore adopted this period for all this work.

In making such digestions, a temperature of 60° is often used, but as we are dealing with products which in practice are to be used at the temperature of the body, generally, it is preferable to take a temperature of 40° as the standard, and this I have done.

Practical Details.

In working this method we need first a standard starch paste. This is made by weighing out enough of the starch, prepared as above, to correspond to 20 grams of pure anhydrous starch. Of 90 per cent. starch we take, therefore, 22.22 grams. This is stirred up to make a uniform cream with 100 cc. of water, and the mixture is then poured into 800 cc. of boiling distilled water, in a flask. The boiling is continued ten minutes and then more water is added to make 1000 grams by weight. The mixture is heated and shaken to distribute the starch uniformly. The contents of the flask should be practically clear and free from all lumps.

For each test quantities of 50 grams each are weighed into a series of 250 cc. flasks, clamped in a large water-bath kept at 40°.

The iodine test solution is made by dissolving 2 grams of iodine and 4 grams of potassium iodide in 250 cc. of water. Two cc. of this solution are then diluted with distilled water to make 1000 cc.

In making up the diastase solutions, the operator must be guided by the results of a few preliminary experiments in each case. For liquid malt extracts, for example, 10 cc. diluted to 100 cc. will be generally a proper strength, while in the examination of the dry preparations on the market, 200 to 500 milligrams dissolved or suspended in 100 cc. of distilled water will usually answer. These solutions are used in this way. Small definite volumes of the dilution are added to the flasks containing the starch paste in the thermostat, and with the least possible loss of time. The mixture is well shaken. The volumes added may be as follows, but all diluted to that of the largest volume before mixing: 1 cc., 2 cc., 3 cc., 4 cc., 5 cc., 6 cc. In about eight minutes tests are begun by removing volumes of 5 drops of each digesting mixture by a pipette and adding this to 5 cc. of the diluted iodine solution in a clear white test tube standing over white paper. It is best to have a row of these tubes mounted to receive the liquids to be tested. If at the end of ten minutes drops from one of the flasks fail to give the iodine reaction, we are ready for a second and more accurate test. Weigh out now 100 grams of the paste into each of 6 bottles and, assuming that the end point was found in the first test to be between 4 and 5 cc., add accurately to the different flasks these volumes of the diastase solution: 8 cc., 8.4 cc., 8.8 cc., 9.2 cc., 9.6 cc., 10 cc. These volumes should stand ready and all diluted to 10 cc. so that they may be poured into and shaken up with the starch without delay. The tests with the iodine solution are repeated as in the first trial and new limits are found between which the real value must lie. For example, at the expiration of ten minutes the paste to which 8.8 cc. of the diastase solution are added may show a faint yellowish dextrin color, while that with the 9.2 cc. is colorless. For all of our practical purposes it is not necessary to go beyond this. In fact, we cannot carry our readings to a much greater degree of accuracy because of the difficulty in distinguishing between the final shade from the disappearing erythrodextrin and the achroodextrin, using these terms in a general sense, rather than in the sense of assuming the actual existence of these forms.

Much of the uncertainty in the determination of diastatic values, as found in the literature, doubtless comes from the failure to recognize the importance of working to a colorless end point whenever this is possible. Roberts[1] pointed this out clearly in his work, but his suggestions

[1] *Loc. cit.*

have been generally overlooked, because perhaps they were made in the course of physiological, rather than in the usual technical, investigations. Most results for starch-converting power which we find advertised are evidently obtained by working to a rose-red end point, as the Pharmacopoeia allows in the case of the pancreatin test. For this reason many of the strong products which I have examined appear to be somewhat weaker than claimed. This is shown by the results of the following table, in which the statements of digesting power are given in both ways. The diastase products tested are among the best known in the market and are widely advertised. In giving the starch-converting power of such preparations anhydrous starch does not appear to be taken as the standard in any case. Average commercial starch contains about 15 per cent. of water, which should be allowed for in making fair comparisons.

TABLE OF STARCH-CONVERTING POWERS.

No.	Value in anhydrous starch, to colorless end point.	Value in anhydrous starch, to loss of blue color.	Value in commercial starch, to loss of blue color.	Value as claimed.
1	100.0	143.0	168.0	150.0
2	16.0	22.5	26.0	150.0
3(liq.)	0.0	0.0	0.0	7+
4	113.	170.0	203.0	200.0
5(liq.)	3.6	5.2	6.1	8.0
6(liq.). .	6.0	8.6	10.1	.....
7(liq.)	6.0	8.6	10.1	.....

The values given in the last column are those claimed by the respective manufacturers, and are based apparently on digestion to the loss of the blue color only. From the advertising literature it is seldom possible to discover the exact basis of the valuation. The values in the second column, of the table, expressing the digestion carried to the achromic point, are much more accurate than those in the following column, where the disappearance of the blue color is recorded. It is not possible to judge of this as closely as desirable for a quantitative test.

Sugar Formation.

It is interesting now to note the amounts of sugar formed by these preparations in equal times, and such determinations were made in this manner. Having found the relative values of the preparations, amounts of each sufficient to convert 1 gram of starch to the achromic point in ten minutes were taken and mixed with 50 grams of starch paste. For each substance five tests were made, the flasks being kept in the thermostat through periods of 10, 30, 60, 120 and 180 minutes, respectively. At the end of the proper time a flask was removed, quickly brought to the boiling-point to check further action, and the sugar then determined as maltose by the Fehling titration. The results of these determina-

tions are shown in the following table, for some of the products described above:

MILLIGRAMS OF REDUCING SUGAR CALCULATED AS MALTOSE, FROM I GRAM OF ANHYDROUS STARCH.

	10 minutes.	30 minutes.	60 minutes.	120 minutes.	180 minutes.
1	613	788	866	866	866
2	611	822	933	1042	1094
3(liq.)	Inert.	Too weak to measure.			
4*a*	622	783	850	855	855
4*b*	630	788	845	858	858
6*a*	633	777	863	872	872
6*b*	635	777	866	866	866

In this table, as in the other, numbers 2 and 3 are preparations from a fungus. Numbers 1, 4 and 6 are pancreas preparations from three different firms, 4*a* and 4*b* are products of one firm purchased some months apart, while 6*a* and 6*b* are products of another firm bought at different times. It is interesting to note that the different products resemble each other very closely in their behavior, and that in all cases the amount of actual sugar formed in ten minutes, that is when the achromic point is reached in the iodine test, is about 60 per cent. of the theoretically possible complete amount, assuming that 1 gram of starch should yield 1.055 grams of maltose. At the end of one hour the amounts have gone up to over 80 per cent. of the possible, and beyond this there is practically no change.

The behavior of the preparation from the fungus is interesting. While its converting power for a short interval is like that of the others, the conversion becomes relatively stronger with time, and evidently proceeds beyond the production of maltose. The results of the calculations from the titrations must be interpreted in this way. It must be remembered, however, that the weight of the preparation required to convert starch with rapidity is much greater than with the other ferments used.

The above results are entirely in accord with those which have been found from time to time for the diastase from malt. A complete conversion is not practically possible, although by precipitating out the dextrins and adding fresh ferment it may be carried somewhat farther than is here done. The values here obtained are easily comparable with those of the iodine method.

The diastase preparations used in the above tests were all practically free from sugar to begin with. But we have as commercial articles a class of products made from malt by various extraction processes in which there is always a large amount of sugar, from the malt, and frequently added glucose. The examination of these mixtures, which are usually in the form of thick sirups, presents greater difficulties. Some

of these articles I have now in hand and expect to report on them at a later time.

NORTHWESTERN UNIVERSITY MEDICAL SCHOOL,
CHICAGO, ILL.

THE SEPARATION OF CLAY IN THE ESTIMATION OF HUMUS.

BY C. A. MOOERS AND H. H. HAMPTON.

Received March 6, 1908.

That a serious error may be introduced into the estimation of humus by the official method has been pointed out by a number of investigators. The chief cause of this error has been the weighing of clay with the humus extract and the consequent reckoning of the combined water in the clay as humus. To avoid this difficulty, Cameron and Breazeale[1] filtered the extract through a Pasteur-Chamberland filter and determined the humus in the clear filtrate; Peter and Averitt[2] have suggested the use of a factor with which to make a correction for the loss in the clayey residue; and a third, or evaporation method has been used by the authors.[3] This paper presents a comparison of the results obtained by the three methods.

In the filtration method the ammoniacal humus extract is filtered through a Pasteur-Chamberland filter, which retains all the clay, and the humus is estimated as usual, by evaporation, etc., of the clear filtrate. In getting the results here reported, a silver-plated, containing tube was used on account of the ready solubility in ammonia of the copper of the usual brass tube.

By the factor method Peter and Averitt make a deduction from the total loss in weight of 10 per cent. of the residue left after the humus has been burnt off. In Table I are given the results obtained by making both a 10 per cent. and a 14 per cent. deduction.

In the evaporation method the ammoniacal humus extract containing clay in suspension is evaporated to dryness over a steam bath, by which means the clay is flocculated so that after extraction with 4 per cent. ammonia it can be retained on a common filter paper. Two evaporations and filtrations are necessary as a rule in order to get a clear filtrate, in which the humus is determined as usual.

The percentages in the first column, obtained with clay present, are not only liable to be irregular, as is shown under 636, but are undoubtedly too high even when the clay is allowed to settle out for several weeks before taking out the aliquot portion for evaporation, as was done for Nos. 602 and 666.

[1] THIS JOURNAL, 26, 29–45.
[2] *Ky. Sta. Bull.*, No. 126, pp. 63–126.
[3] *Tenn. Sta. Bull.*, Vol. 19, No. 4, p. 50.

TABLE I.—PER CENT. OF HUMUS ESTIMATED BY THE DIFFERENT METHODS IN REPRESENTATIVE TENNESSEE SOILS.

Soil No.	Character of soil.		With clay present.	Residue after burning.	Correction method. (1) Factor 10.	Correction method. (2) Factor 14.	Filtration method.	Residue after burning.	Evaporation method.	Residue after burning.
636	Fertile clay loam....	1	2.04	5.23	1.52	1.31	0.64	0.22	1.36	0.28
		2	2.34	6.75	1.66	1.40	0.65	0.18	1.33	0.19
		3	2.64	7.97	1.84	1.51	0.77	0.21	1.38	0.23
		4	2.55	8.78	1.67	1.32	0.59	0.24	1.26	0.33
602	Poor clay loam.....	1	1.28	1.95	1.08	1.01	0.76	0.23	1.08	0.29
		2	1.26	2.06	1.05	0.97	....	....	1.11	0.18
666	Silt loam	1	1.19	2.01	0.99	0.91	0.53	0.12	0.82	0.09
		2	1.13	1.68	0.96	0.89	....	....	0.88	0.25
584	Rich loam.....		2.54	5.68	1.97	1.74	....	....	1.67	0.49
577	Rich loam.....		3.07	7.91	2.28	1.96	....	....	1.77	0.65
									1.73	0.50
									1.72	0.69

The correction method undoubtedly gives better results than the preceding, but the duplications of Nos. 636 are not concordant, and there is a question as to the proper factor. For these soils a 14 per cent. rather than a 10 per cent. correction gives the most harmonious results.

The filtration method proved highly unsatisfactory, chiefly on account of the humus absorbed by the filter. No simple way to avoid this defect was found. The first three results on No. 636 were obtained from successive filtrations of the same solution. These filtrations were made after the first runnings had been discarded. Each of the after parts that were analyzed represented about one-third of the remaining liquid. The fact that by the evaporation method, in which perfectly clear solutions were obtained, the results were, in round numbers, from 40 to 100 per cent. greater than those gotten by the use of the filter, is conclusive evidence of the inadequacy of the filtration method.

The evaporation method yielded at least fairly concordant results, but as they were obtained in the early part of our work they are probably not as uniform as the method will permit under close attention to details.

In Table II are given the percentages of humus by the evaporation method, and of total nitrogen by the Kjeldahl method, found in adjacent plots of an experimental field at the Tennessee Experiment Station farm. Lime had been applied to one-half of each of the plots at the rate of 1800 pounds per acre three years before the samples were taken for analysis. The results indicate that by the aid of this simple modification small changes in the humus-content of a soil can be measured.

TABLE II.—EFFECT OF LIMING ON THE HUMUS AND NITROGEN CONTENTS OF SOILS FROM ADJACENT PLOTS.

Plot No.	Fertilized with	Limed half. Humus. Per cent.	Limed half. Nitrogen. Per cent.	Unlimed half. Humus. Per cent.	Unlimed half. Nitrogen. Per cent.
F4	Mineral Fertilizer	1.28	0.119	1.32	0.119
F5	" "	1.38	0.121	1.42	0.129
F6	Farmyard manure	1.47	0.131	1.47	0.136
F8	Mineral fertilizer	1.37	0.126	1.41	0.126
G4	" "	1.32	0.122	1.37	0.119
G5	" "	1.33	0.118	1.34	0.125
G6	Farmyard manure and mineral fertilizer	1.39	0.126	1.42	0.131
G8	Mineral fertilizer	1.04	0.100	1.10	0.108
	Average	1.32	0.120	1.36	0.124

TENNESSEE AGRICULTURAL EXPERIMENT STATION,
KNOXVILLE, TENN., March 4, 1908.

(CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 151.)

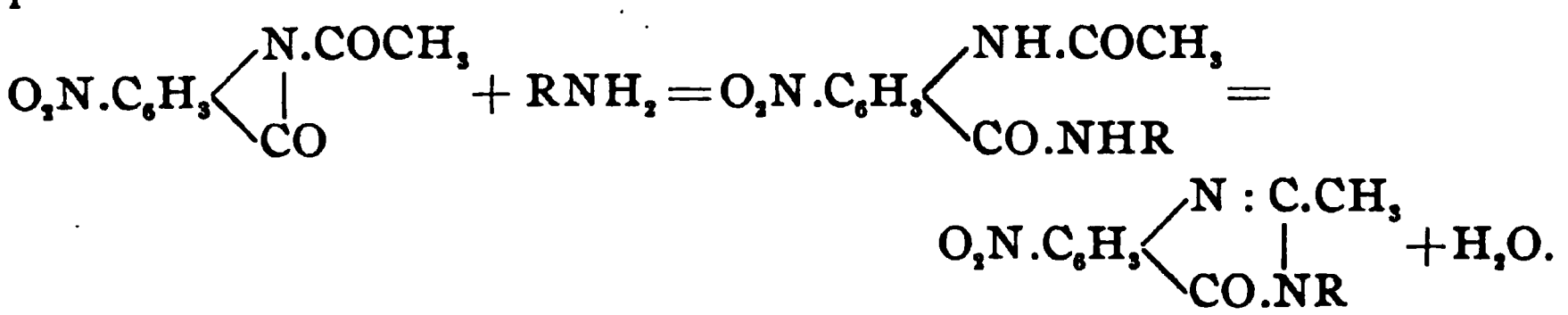
RESEARCHES ON QUINAZOLONES (TWENTIETH PAPER) ON CERTAIN 7-NITRO-2-METHYL-4-QUINAZOLONES FROM 4-NITROACETANTHRANIL.[1]

BY MARSTON TAYLOR BOGERT AND WILLIAM KLABER.

Received Febuary 28, 1908.

Bogert and Steiner[2] and Bogert and Seil[3] have already reported on the synthesis of 7-nitro-2-methyl-4-quinazolones from 4-nitroacetanthranil and various primary amines by the Anschütz, Schmidt and Greiffenberg[4] reaction. The present paper records the continuation and extension of this work.

The reacion involved is a simple one, and may be conveniently expressed as follows:



In one or two cases we isolated the intermediate amide.

The primary monamines used were ammonia, methyl-, *n*-propyl-, benzyl- and β-naphthylamines, aniline and *p*-anisidine. All of these

[1] Read at the General Meeting of the American Chemical Society, December 28, 1906.

[2] THIS JOURNAL, 27, 1327 (1905).

[3] *Ibid.*, 29, 517 (1907).

[4] *Ber.*, 35, 3480 (1902).

condensed smoothly with the acetanthranil, giving good yields and clean products.

It was also found possible to condense the anthranil with amino nitriles and amino acid esters, but not with the free amino acid or its salts. Glycine ester and nitrile and anthranilic ester and nitrile were used in the experiments, and the corresponding quinazolones obtained. By the hydrolysis of the quinazolone nitriles, or by the action of ammonia upon the quinazolone esters, the corresponding amides were prepared. And from the latter, in turn, the nitriles were regenerated by the action of acetic anhydride.

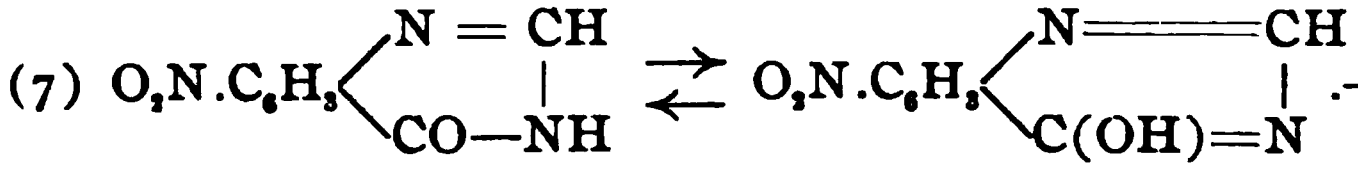
With hydrazine, both the 3-aminoquinazolone and the corresponding diquinazolonyl were obtained.[1] From the amino compound, acetyl and di-acetyl derivatives were prepared, as well as the phenylhydrazone of the monacetyl compound. By the Bülow condensation[2] with ethyl diaceto succinate, the pyrrole compound was produced.

7-Nitro-4-quinazolone (7-nitro-4-hydroxyquinazoline) was prepared from 4-nitro-2-aminobenzoic acid and formamide,[3] and 7-amino-2-methyl-4-quinazolone by reducing the corresponding nitro compound.

Experimental.

4-Nitroacetanthranil was prepared, as described by Bogert and Steiner,[4] by nitrating *o*-toluidine in presence of excess of concentrated sulphuric acid, acetylating the 4-nitro-2-toluidine, oxidizing the nitroacettoluidide to the nitro acetaminobenzoic acid, and converting the latter into the corresponding nitroacetanthranil by the action of acetic anhydride.

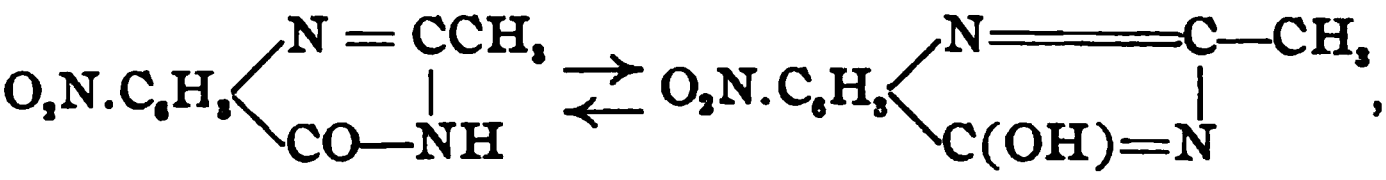
7-Nitro-4-quinazolone (7-Nitro-4-hydroxyquinazoline),



(7) $O_2N.C_6H_3\langle{}^{N=CH}_{CO-NH} \rightleftarrows O_2N.C_6H_3\langle{}^{N=\!=\!=CH}_{C(OH)=N}$.—4-Nitro-2-aminobenzoic acid was gently fused with excess of formamide, giving a dark red solution. After removal of the excess of formamide, the residue was purified by treating with boneblack and crystallizing from alcohol. Long, slender, glistening yellow needles m. p. 276° (cor.).

Nitrogen found, 22.21. Calculated for $C_8H_5O_3N_3$: N, 22.0.

7-Nitro-2-methyl-4-quinazolone(7-Nitro-2-methyl-4-hydroxyquinazoline),



$O_2N.C_6H_3\langle{}^{N=CCH_3}_{CO-NH} \rightleftarrows O_2N.C_6H_3\langle{}^{N=\!=\!=C-CH_3}_{C(OH)=N}$, has been reported previously by Bogert and Steiner[4] and Bogert and Seil.[4] By care-

[1] Compare Bogert and Seil, THIS JOURNAL, 28, 884 (1906); Bogert and Cook, *Ibid.*, 28 1453 (1906).

[2] *Ber.*, 35, 4312 (1902); 39, 2621, 3372 (1906).

[3] Niementowski, J. *prakt. Chem.* [2], 51, 564 (1895).

[4] *Loc. cit.*

ful purification, we have succeeded in raising the melting-point from 275–7° (as given by them) to 287–90° (cor.). As thus purified, the substance forms silky needles of a pale greenish cast. It was prepared both from the anthranil and ammonia, and by the action of heat upon the ammonium salt of 4-nitro-2-acetaminobenzoic acid. It dissolves in neutral sodium carbonate solutions with evolution of carbon dioxide, but can be reprecipitated from this solution by saturating with carbon dioxide, as it is insoluble in the acid carbonate. It is also soluble in concentrated aqueous ammonia, but reprecipitates when the solution is boiled. It crystallizes unchanged from fused ammonium acetate. Stannous chloride reduces it to the 7-amino compound (described beyond).

Oxidation of 7-Nitro-2-methyl-4-quinazolone.—Seven grams of the quinazolone were dissolved in 300 cc. dilute sulphuric acid (one of concentrated acid to five of water) containing 14 grams chromic anhydride, and the solution boiled for about 60 hours. On cooling, small, colorless crystals separated. Dissolved in sodium carbonate solution, reprecipitated by acetic acid, and recrystallized from alcohol, colorless scales were obtained, melting at about 327° (uncor.), and dissolving with a red color in caustic or carbonated alkali solutions. Not enough of the substance was obtained for an analysis.

Potassium Salt of 7-Nitro-2-methyl-4-hydroxyquinazoline.—The quinazoline was dissolved in dilute potassium hydroxide solution and this solution then saturated with solid potassium carbonate. The yellow precipitate was filtered out, dissolved in absolute alcohol, and the filtered solution evaporated to dryness, leaving a pale yellow crystalline mass easily soluble in water or alcohol. It crystallizes from alcohol with alcohol of crystallization as a pale yellow solid, the color deepening to an orange on driving out the alcohol. It was analyzed by titration with fifth-normal sulphuric acid, using phenolphthalein as indicator.

Potassium found, 16.21. Calculated for $C_9H_6O_3N_2K$: K, 16.11.

Silver Salt.—The quinazoline was dissolved in concentrated aqueous ammonia, the solution heated to boiling, and ammoniacal silver nitrate solution added gradually as long as it gave a precipitate. The precipitate was voluminous and curdy, and of a faint yellow color. It was washed thoroughly with dilute ammonia water and dried. It is decomposed quantitatively when heated with a salt solution. Analyzed in this way, it gave the following result:

Silver found, 34.35. Calculated for $C_9H_6O_3N_2Ag$: Ag, 34.60.

7-Nitro-2,3-dimethyl-4-quinazolone, $O_2N.C_6H_3\left\langle\begin{array}{l} N:C.CH_3 \\ \quad\quad | \\ CO.NCH_3 \end{array}\right.$.—Bogert and Steiner[1] prepared this substance by the action of methylamine upon the

[1] *Loc. cit.*

4-nitroacetanthranil. We have also obtained it by heating the methylamine salt of 4-nitroacetanthranilic acid at 190–200°, but the yield by this latter method is poor and the product quite impure. It is unchanged by fusion with ammonium acetate or by heating with ammonium formate for three hours in a sealed tube at 230°. Bogert and Steiner describe the compound as forming light yellowish green crystals, m. p. 144–5° (cor.). We have succeeded in getting it nearly colorless and of a m. p. 151–2° (cor.).

7-Nitro-2-methyl-3-n-propyl-4-quinazolone, from 4-nitroacetanthranil and *n*-propylamine, crystallizes from dilute alcohol in colorless needles, m. p. 140° (cor.). It is slightly soluble in water and soluble in alcohol.

Nitrogen found, 16.9. Calculated for $C_{12}H_{13}O_3N_3$: N, 17.0.

7-Nitro-2-methyl-3-phenyl-4-quinazolone, from the nitroacetanthranil and aniline, crystallizes from alcohol in nearly colorless, diamond-shaped plates, m. p. 209° (cor.).

Nitrogen found, 14.82. Calculated for $C_{15}H_{11}O_3N_3$: N, 14.94.

7-Nitro-2-methyl-3-benzyl-4-quinazolone, from the nitroacetanthranil and benzylamine, crystallizes from alcohol in coarse, yellowish, cubical forms, m. p. 131–2° (cor.).

Nitrogen found, 14.27. Calculated for $C_{16}H_{13}O_3N_3$: N, 14.23.

Its *hydrochloride* forms pale yellowish crystals, m. p. 229–30° (cor.), which lose their HCl when boiled with alcohol.

Nitrogen found, 12.92. Calculated for $C_{16}H_{14}O_3N_3Cl$: N, 12.67.

7-Nitro-2-methyl-3-p-anisyl-4-quinazolone, from the nitroacetanthranil and *p*-anisidine, crystallizes from alcohol in glistening scales, of a faintly yellowish cast, m. p. 228° (cor.).

Nitrogen found, 13.49. Calculated for $C_{16}H_{13}O_4N_3$: N, 13.50.

7-Nitro-2-methyl-3-β-naphthyl-4-quinazolone, from the nitroacetanthranil and β-naphthylamine. Fine, colorless needles (from alcohol), m. p. 218–9° (cor.).

Nitrogen found, 12.64. Calculated for $C_{19}H_{13}O_3N_3$: N, 12.68.

7-Amino-2-methyl-4-quinazolone (*7-amino-2-methyl-4-hydroxyquinazoline*).—The 7-nitro compound was reduced with stannous chloride and hydrochloric acid. The double chloride of tin and the amino quinazoline which separated was boiled with dilute sodium carbonate solution and filtered hot. On cooling, the 7-aminoquinazoline separated from the filtrate in long, silky, colorless needles, m. p. 311° (cor.), identical with the quinazoline obtained by the action of potassium hydroxide solution upon 7-acetamino-2-methyl-4-quinazolone (which will be described in another paper). It is soluble in hot water, alcohol or caustic alkali solutions, but not in cold sodium carbonate solutions. Crystals obtained from water or alcohol carry approximately half a molecule of the solvent.

Nitrogen found, 24.22. Calculated for $C_9H_9ON_3$: N, 24.0.

7-Nitro-2-methyl-3-amino-4-quinazolone. — 4-Nitroacetanthranil was added gradually to an excess of 50 per cent. hydrazine hydrate solution (aqueous). Considerable heat was developed and the reaction was completed by further final warming. When cold, the insoluble product was extracted with a small amount of alcohol, to remove nitroanthranilic acid and small amounts of impurities, and the residue was then purified by crystallization from alcohol. Shining, pale yellow needles, m. p. 223° (cor.). With acetic anhydride it gives both mono- and diacetyl derivatives.

Nitrogen found, 25.73 and 25.74. Calculated for $C_9H_8O_3N_4$: N, 25.45.

The yield of pure aminoquinazolone was generally about 50 per cent. of the theory.

7-Nitro-2-methyl-3-amino-4-quinazolone and phenylhydrazine.—The amino quinazolone was mixed with excess of phenylhydrazine and the mixture heated just to boiling. As soon as ebullition began, the flame was removed, as considerable heat is developed by the reaction. Ammonia was evolved. When the action moderated, the heating was renewed for a short time, the mass allowed to cool somewhat, excess of acetic acid added and the mixture warmed up again. This second phase of the reaction also proceeds with considerable rise of temperature, due to the combination of the acetic acid with the excess of phenylhydrazine and the formation of acetylphenylhydrazide, and the flame should be removed as soon as the reaction threatens to become violent. The dark colored product is heated for a short time further, concentrated to small volume and allowed to crystallize. The mixture is diluted largely with cold water, the insoluble material crystallized from alcohol and washed with ether. From very dilute potassium hydroxide solution it separated in fine needles, which were recrystallized from alcohol, giving clusters of colorless, feathery needles, m. p. 230° (uncor.), insoluble in ether, soluble in hot water, easily soluble in alcohol.

Found: C, 48.62 and 48.82; H, 5.9 and 5.52; N, 25.60 and 25.54.

These figures are far removed from those calculated for the phenylhydrazinoquinazolone, the phenylhydrazinophenylhydrazone, or the osotetrazole which might be formed from the latter by loss of a molecule of aniline. The compound has not been identified.

A similar product was obtained by heating the amino quinazolone with two molecules of phenylhydrazine in cumene solution, water and ammonia being evolved. When the heating was conducted in nitrobenzene or alcoholic acetic acid solution, but little action took place.

7-Nitro-2-methyl-3-acetamino-4-quinazolone.—The above quinazolone, when heated with acetic anhydride, gave a clear solution. This solution was concentrated to crystals, which were washed with carbon tetrachloride and recrystallized from benzene. Short, colorless prisms, m.

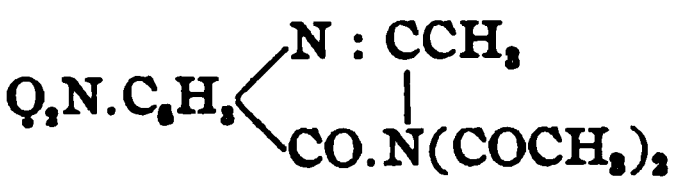
p. 233° (cor.), soluble in alcohol, insoluble in carbon tetrachloride, and but sparingly soluble in cold benzene.

Nitrogen found, 21.49. Calculated for $C_{11}H_{10}O_4N_4$: N, 21.37.

Phenylhydrazone.—The acetaminoquinazolone and phenylhydrazine were heated just to boiling and the flame removed. If large amounts are used, the reaction proceeds with considerable violence and frothing. On cooling, the mass solidified. It was washed with ether and crystallized from alcohol. Beautiful, glassy prims, m. p. 315° (cor.).

Found: C, 57.80; H, 4.90; N, 23.4. Calculated for $C_{17}H_{16}O_3N_6$: C, 57.95; H, 4.54; N, 23.86.

7-Nitro-2-methyl-3-diacetamino-4-quinazolone,

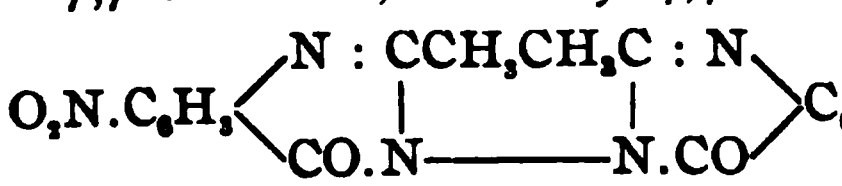


$O_2N.C_6H_3\langle N:CCH_3 / CO.N(COCH_3)_2\rangle$.—This was obtained from either the amino or acetaminoquinazolone by the further action of acetic anhydride. The diacetyl compound is much more soluble in benzene than the monacetyl and the two can be separated in this way. The diacetyl derivative was separated from the benzene mother liquors by careful addition of gasoline. It crystallizes in pale yellow, glassy plates, m. p. 132° (cor.), soluble in alcohol, benzene, or acetic anhydride. Oxidation with neutral permanganate yielded only 4-nitroanthranilic acid and its acetyl derivative.

Nitrogen found, 18.79 and 18.89. Calculated for $C_{13}H_{12}O_5N_4$: N, 18.42.

When the diacetyl derivative was boiled with phenylhydrazine in alcoholic acetic acid solution, the only change noted was the formation of the monacetyl compound. No hydrazone was observed. A boiling alcoholic solution of aniline had the same effect in changing the diacetyl to the monacetyl derivative.

7,7′-Dinitro-2,2′-dimethyl-4,4′-diketotetrahydro-3,3′-diquinazolyl,



$O_2N.C_6H_3\langle N:CCH_3CH_3C:N / CO.N——N.CO\rangle C_6H_3.NO_2$.—One gram of 50 per cent. aqueous hydrazine hydrate solution was added to 6.4 grams 4-nitroacetanthranil and the mixture heated for a short time on the sand-bath. When cold, the solid product was extracted with dilute acetic acid, to remove aminoquinazolone, and the residue crystallized from a mixture of ethyl and isoamyl acetates. Small, yellow, granular crystals, m. p. 337.5° (cor.). The yield was poor.

Nitrogen found, 20.63. Calculated for $C_{18}H_{12}O_6N_6$: N, 20.58.

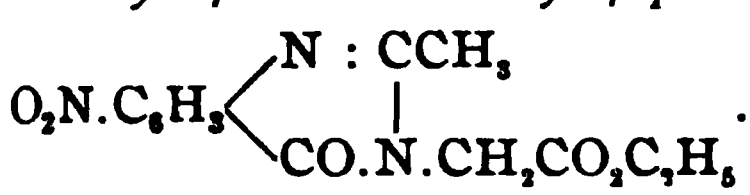
The substance is soluble in ethyl or isoamyl acetates, but is insoluble in water, alcohol, and in the majority of the ordinary organic solvents. It dissolves in acetic anhydride and, on cooling, white crystals separate,

m. p. 227° (uncor.). probably similar to the acetic anhydride addition-product described by Bogert and Seil[1] for the corresponding 5,5′-dinitro-diquinazolyl.

4-Nitroacetanthranil and Guanidine.—When these substances were heated together in aqueous solution, in equal molecules, the guanidine salt of 4-nitroacetanthranilic acid was obtained. It forms coarse, lentil-shaped crystals, m. p. 247° (cor.).

In one case, where two molecules of the anthranil were used to one of the guanidine, a small amount of a yellow substance was isolated, which melted sharply at 253°, resolidified and did not re-melt below 300°. It was not obtained in sufficient amount to identify.

Ethyl 7-Nitro-2-methyl-4-quinazolonyl-3-acetate,



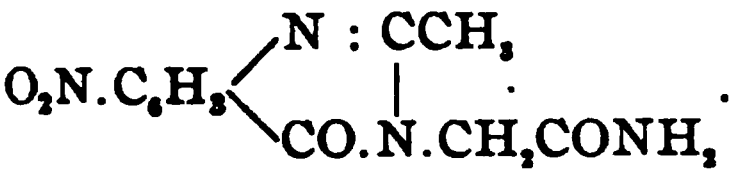
.—Attempts to condense 4-nitroacetanthranil with free glycine or with its sodium salt failed. Heating with aqueous solutions caused only hydrolysis of the anthranil, while direct dry heating resulted in decomposition.

Three and one-half grams glycine ester hydrochloride were dissolved in the smallest possible amount of water and the hydrochloric acid removed by the addition of the moist silver oxide from 4.66 grams of silver nitrate. Five grams of the anthranil were then added to the mixture, and the temperature raised rapidly to the boiling-point. The close of the reaction was indicated by the clearing of the solution, followed by the appearance of turbidity in the supernatant liquid. The quinazolone ester was extracted with ether and purified by crystallization from the same solvent. Asbestos-like sheaves of colorless crystals, m. p. 139–40° (cor.).

Nitrogen found, 14.38. Calculated for $C_{13}H_{13}O_5N_3$: N, 14.43.

After the ether extraction, the residual solution was found to contain some nitroacetanthranilic acid.

7-Nitro-2-methyl-4-quinazolonyl-3-acetamide,



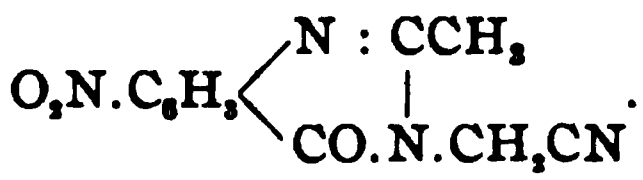
.—The above ethyl ester was boiled with excess of concentrated aqueous ammonia until a clear solution was obtained. On cooling, colorless, very fine, silky needles separated. Recrystallized from alcohol, they showed a m. p. of 275° (cor.).

Nitrogen found, 21.45. Calculated for $C_{11}H_{10}O_4N_4$: N, 21.37.

When boiled with acetic anhydride, it gave the nitrile described below.

7-Nitro-2-methyl-4-quinazolonyl-3-acetonitrile,

[1] THIS JOURNAL, 28, 892 (1906).



.—4-Nitroacetanthranil and anhydrous acetonitrile were found to be without action upon each other at the boiling-point of the nitrile (81°) or in a sealed tube at 160°.

4.17 grams potassium hydroxide were dissolved in a small amount of water, the solution cooled in an ice pack, and 5.78 grams aminoacetonitrile sulphate (50 per cent. excess) added slowly with stirring, care being taken to prevent any considerable rise of temperature. Five grams nitroacetanthranil were then quickly stirred in and the mixture heated rapidly to boiling. After boiling for about five minutes, the dark red solution was allowed to cool, cold water added, the mixture thoroughly stirred, and the precipitate filtered out. This was treated with bone-black in acetone solution, and repeatedly crystallized from the same solvent. Colorless, shining scales, m. p. 207–8° (cor.), insoluble in water or petroleum distillates, soluble in alcohol, acetone or dilute acetic acid.

Nitrogen found, 23.10. Calculated for $C_{11}H_8O_3N_4$: N, 22.90.

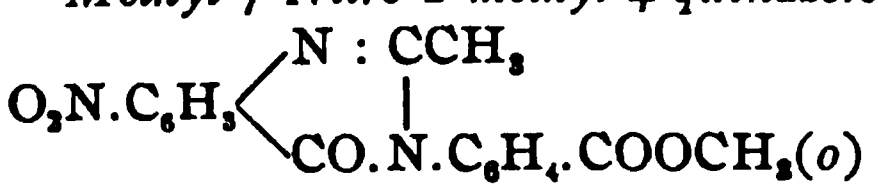
4-Nitro-2-acetaminohippuronitrile,

(4)O_2N(2)$CH_3CONH.C_6H_3.CONHCH_2CN$.—This intermediate amide was found in the acetone mother liquors from the above quinazolone. It is very much more soluble in acetone than the quinazolone and can be separated by this property. It crystallizes in colorless prisms, melting with effervescence at 194° (cor.) (probably changing to the quinazolone), and is readily changed to the quinazolone by heating with very dilute potassium hydroxide solution.

Nitrogen found, 21.53. Calculated for $C_{11}H_{10}O_4N_4$: N, 21.37.

When ethyl β-aminocrotonate and 4-nitroacetanthranil were heated together, only 7-nitro-2-methyl-4-quinazolone (7-nitro-2-methyl-4-hydroxyquinazoline) was obtained. This is, of course, due to the fact that the aminocrotonic ester loses ammonia very readily, and this ammonia then condenses with the anthranil to the simple quinazolone.

Methyl 7-Nitro-2-methyl-4-quinazolonyl-3-o-benzoate,

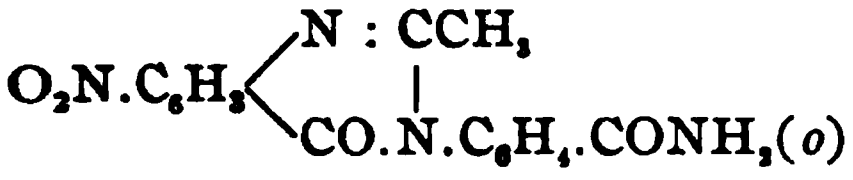


.—Neither anthranilic acid nor its sodium salt could be made to condense with 4-nitroacetanthranil.

The anthranil was heated for a short time with excess of methyl anthranilate and the mixture then allowed to cool. The resultant glassy solid was extracted with alcohol, the alcoholic solution treated with bone-black, and the precipitate which separated on cooling treated with cold dilute potassium hydroxide solution, to remove nitroacetanthranilic acid. The residue, crystallized from alcohol, gave canary-yellow, granular crystals, m. p. 175° (cor.), quite soluble in alcohol, but insoluble in water.

Nitrogen found, 12.52. Calculated for $C_{17}H_{13}O_5N_3$: N, 12.38.

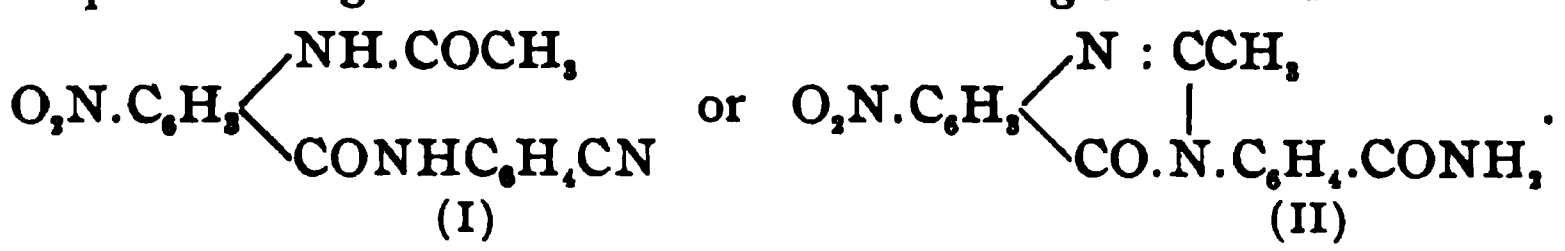
7-Nitro-2-methyl-4-quinazolonyl-3-o-benzamide,



$O_2N.C_6H_3\langle{}^{N:CCH_3}_{CO.N.C_6H_4.CONH_2(o)}$.—Anthranilic nitrile was just covered with water and the mixture heated to boiling. The nitrile remained largely undissolved as a yellow oil. 4-Nitroacetanthranil was then added. The oily nitrile turned dark and finally solidified to a yellow mass, a precipitate also appearing in the supernatant liquid. Potassium carbonate was added to the cold solution, to remove nitroacetanthranilic acid. The residue was then extracted with ethyl acetate, to eliminate certain easily soluble impurities, and the undissolved portion crystallized from nitrobenzene, the excess of solvent being washed out with alcohol. Straw-colored needles, m. p. 320–1° (cor.), soluble in nitrobenzene or acetic anhydride but only moderately soluble in alcohol.

Nitrogen found, 17.34, 17.28 and 17.38. Calculated for $C_{16}H_{12}O_4N_4$: N, 17.3.

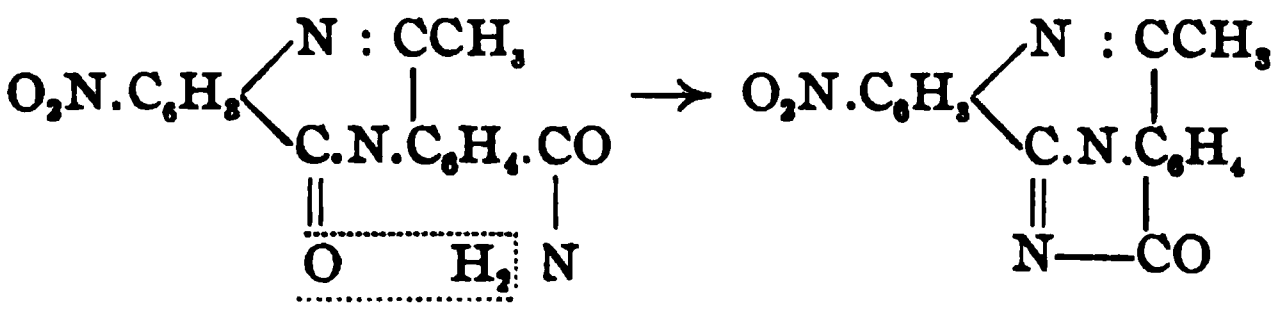
The product might have either of the following structures:



$O_2N.C_6H_3\langle{}^{NH.COCH_3}_{CONHC_6H_4CN}$ (I) or $O_2N.C_6H_3\langle{}^{N:CCH_3}_{CO.N.C_6H_4.CONH_2}$ (II).

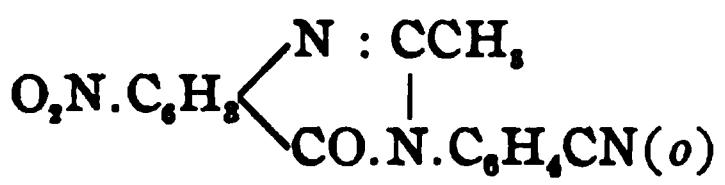
Boiled with acetic anhydride, it gave the benzonitrile quinazolone described below, from which it can also be produced by five to six hours' boiling with alcohol, the conversion being a quantitative one. This dehydration could occur quite readily with either structure, but the easy re-hydration of the benzonitrile quinazolone to the same product would seem to us to exclude formula (I). Further, the compound does not melt and re-solidify below the m. p. of the quinazolone, as is usually the case with such intermediate amides as (I), nor does it change to the quinazolone on long boiling in nitrobenzene as (I) might be expected to do in line with the synthesis of the benzonitrile quinazolone described below.

Attempts to bring about a further condensation, thus:



$O_2N.C_6H_3\langle{}^{N:CCH_3}_{C.N.C_6H_4.CO}$ (O, H_2, N) → $O_2N.C_6H_3\langle{}^{N:CCH_3}_{C.N.C_6H_4}$ (N—CO) were unsuccessful.

7-Nitro-2-methyl-4-quinazolonyl-3-o-benzonitrile,



$O_2N.C_6H_3\langle{}^{N:CCH_3}_{CO.N.C_6H_4CN(o)}$.—Pure benzonitrile was found to be without action upon 4-nitroacetanthranil.

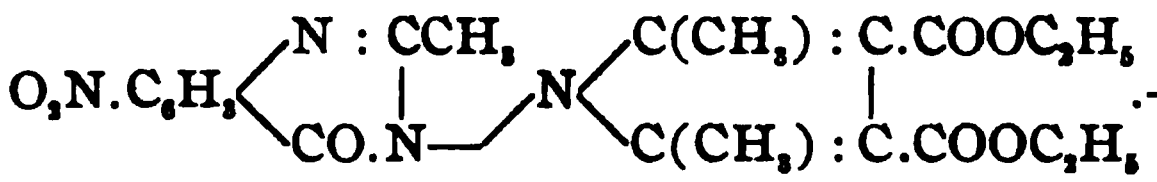
By fusing anthranilic nitrile with the nitroacetanthranil, and extracting the product with ether, heavy red needles were obtained, m. p. 225° (uncor.).

In a second experiment, the condensation was carried out in boiling nitrobenzene solution. The reddish crystals were treated with bone-black in benzene solution, and recrystallized from alcohol. Slender, glistening, yellowish needles, m. p. 234° (cor.); soluble in alcohol, benzene, ether, nitrobenzene or acetic anhydride.

Nitrogen found, 18.23 and 18.45. Calculated for $C_{16}H_{10}O_3N_4$: N, 18.30.

Long boiling with 95 per cent. alcohol changed this compound completely to the amide mentioned above, from which it could, as stated, be regenerated by dehydration with acetic anhydride. As anthranilic nitrile itself is rather resistant to hydrolysis, the ease with which this quinazolone nitrile changes to the amide is rather surprising.

7-Nitro-2-methyl-4-quinazolonyl-3-(2,5-dimethyl-3,4-dicarbethoxypyrrole),



.—Bülow has shown[1] that hydrazines of the type $RNHNH_2$ or R_2NNH_2 condense with diacetosuccinic ester to derivatives of pyrrole.

Three grams of the 3-aminoquinazolone and four of ethyl diacetosuccinate were dissolved in 40 cc. of glacial acetic acid, the solution boiled for three hours, and then concentrated. A small amount of precipitate separated on cooling. This was removed, and alcohol added to the mother liquor. A white precipitate resulted, which was purified by repeated crystallization from alcohol, until it appeared in colorless, shining, minute scales, of a constant m. p. of 171° (cor.).

Found: C, 56.45; H, 4.8; N, 12.86. Calculated for $C_{21}H_{22}O_7N_4$: C, 57.0; H, 4.97; N, 12.67.

HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY,
NEW YORK, February 25, 1908.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

ON THE ACTION OF α-BENZOYLPHENYLHYDRAZINE ON THE HALOGEN DERIVATIVES OF QUINONES,

BY WILLIAM MCPHERSON AND WILBUR L. DUBOIS.

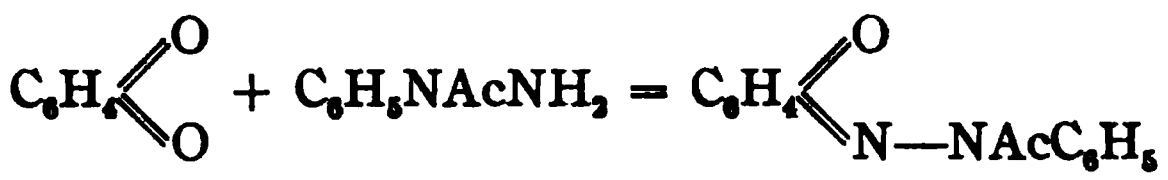
Received March 26, 1908.

The action of phenylhydrazine on quinones was first investigated by Zincke.[2] He showed that phenylhydrazine, as well as its salts, acted

[1] *Loc. cit.*

[2] *Ber.*, 16, 1563.

energetically on the quinones of the benzene series with evolution of gas, but did not isolate the compounds formed. More recently it was shown by one of us, working under the guidance of Dr. J. U. Nef, that if the α-hydrogen in phenylhydrazine is displaced by an acyl group the resulting compounds condense smoothly with benzo- and naphthoquinones in a perfectly normal manner, forming hydrazones.[1] Thus, with benzoquinone, the action is expressed by the following equation:



$$C_6H_4\langle{}^{O}_{O} + C_6H_5NAcNH_2 = C_6H_4\langle{}^{O}_{N-NAcC_6H_5} + H_2O.$$

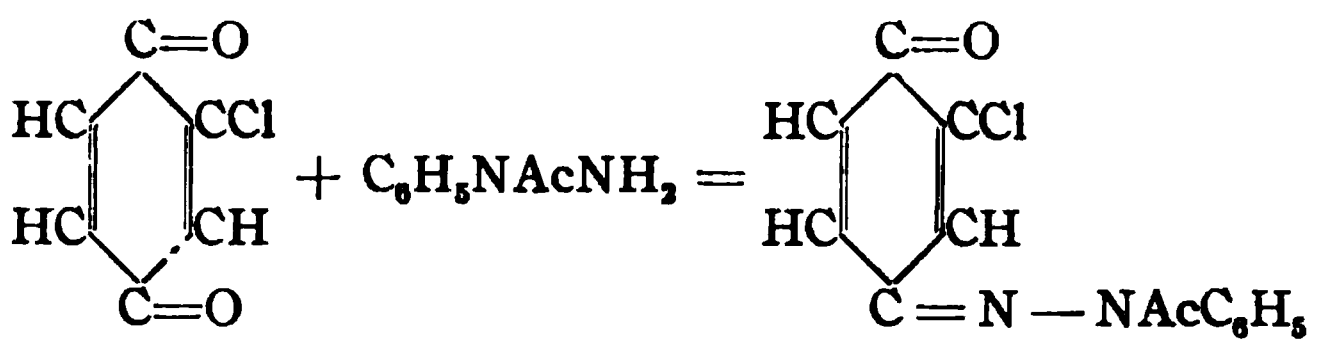
The action of naphthylhydrazine on both benzo- and naphthoquinones has also been studied by McPherson and Gore,[2] and the results of these investigations have had an important bearing in determining the constitution of the hydroxyazo compounds.

Zincke also studied the action of phenylhydrazine on the halogen derivatives of the benzoquinones[3] and found that decomposition occurred, accompanied by evolution of nitrogen. An investigation was begun in this laboratory to determine the action of acylated phenylhydrazines on the halogen derivatives of the quinones, and a preliminary paper was published.[4] Unfortunately the notes on all the work done were destroyed by the burning of the laboratory, and it has been possible only recently to resume again the investigation. Since a number of other investigators are working in this field, the following report is published with the hope that I may be allowed to reserve this phase of the subject for investigation. The action of the α-acylated phenylhydrazines on the more recently discovered orthobenzoquinone, as well as its halogen derivatives, is also being studied with the hope that some light may be thrown on the constitution of the hydroxyazo compounds.

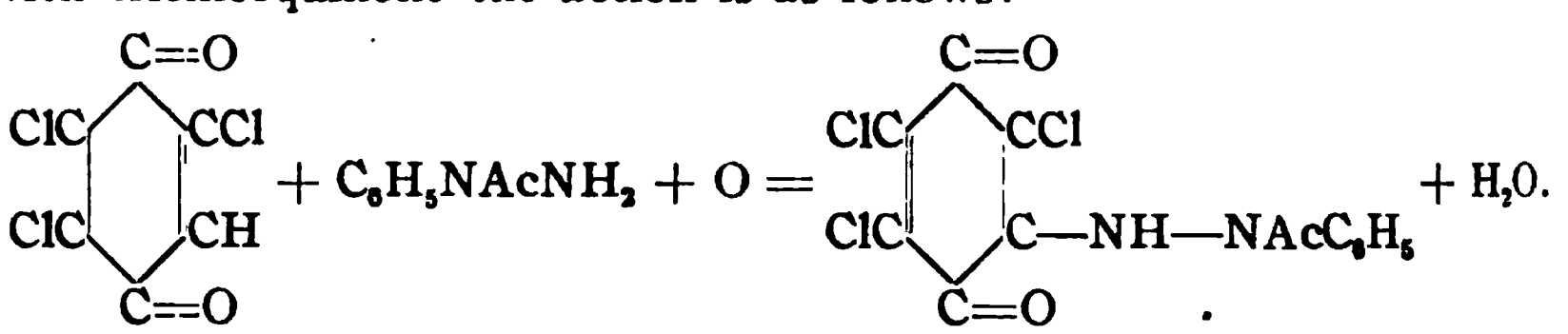
It has been found that the α-acylated phenylhydrazines act on the halogen derivatives of the benzoquinones in three different ways, as follows:

1. A regular condensation may take place with the formation of hydrazones. One would naturally expect this reaction with the monohalogenated quinones, since it is with thse derivatives that hydroxylamine most readily condenses to form oximes. So far as the experiments have been carried out, it is only with these derivatives that hydrazones are formed. With monochlorbenzoquinone the reaction is expressed as follows:

[1] *Ber.*, 28, 2414; *Am. Chem. J.*, 22, 364.
[2] *Am. Chem. J.*, 25, 485.
[3] *Ber.*, 16, 1563.
[4] THIS JOURNAL, 22, 141.

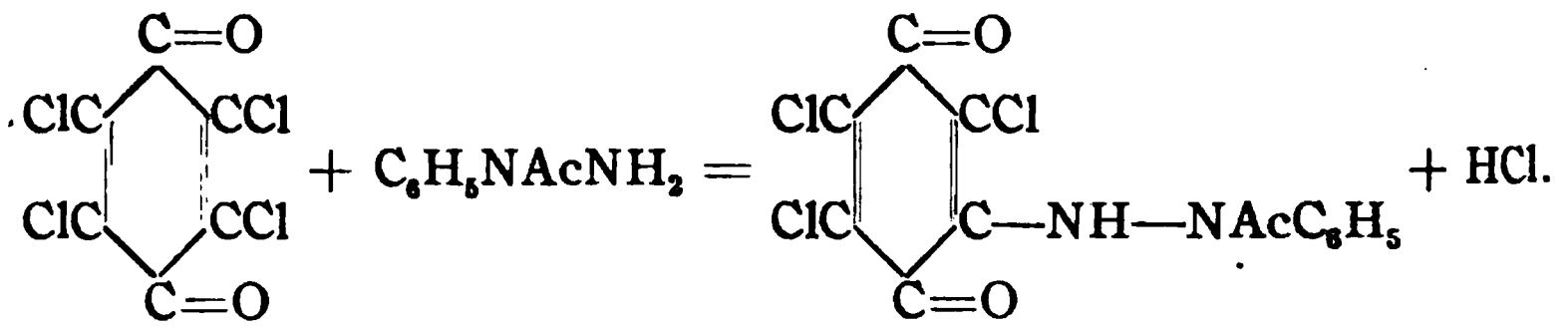


2. One of the hydrogen atoms in the NH_2 group of the hydrazine, together with one of the atoms of the quinone hydrogen, may be removed by the oxidizing action of a second molecule of the quinone. Thus with trichlorquinone the action is as follows:



This reaction is in accord with the fact that hydroxylamine, which readily forms oximes with the monohalogenated quinones, does not do so with the trihalogen derivatives.

3. One of the hydrogen atoms in the NH_2 group of the hydrazine may combine with a chlorine atom of the quinone, splitting off hydrochloric acid. Thus, with tetrachlorquinone, the reaction is expressed by the following equation:



Experimental Part.

Action of α-Benzoylphenylhydrazine on Monochlorbenzoquinone. Monochlorquinonebenzoylphenylhydrazone,

$O = C\langle^{CCl = CH}_{CH = CH}\rangle C = N—NC_7H_5OC_6H_5$.—The chlorquinone was prepared from chlorhydroquinone by Clark's method.[1] Twenty-five grams of the chlorhydroquinone gave 20 grams of the chlorquinone when treated with the reagents in the following proportion: Chlorhydroquinone 25 g., manganese dioxide 36 g., water 125 cc., sulphuric acid 25 cc.

Five and four-tenths grams of the chlorquinone and 10 grams of α-benzoylphenylhydrazine sulphate were dissolved by heating in separate portions of a mixture of 200 cc. of alcohol and 50 cc. of water. The solutions were cooled to room temperature and then mixed and heated slowly on a water-bath to from 50° to 60°, the mixture being stirred occasion-

[1] *Am. Chem. J.*, 14, 555.

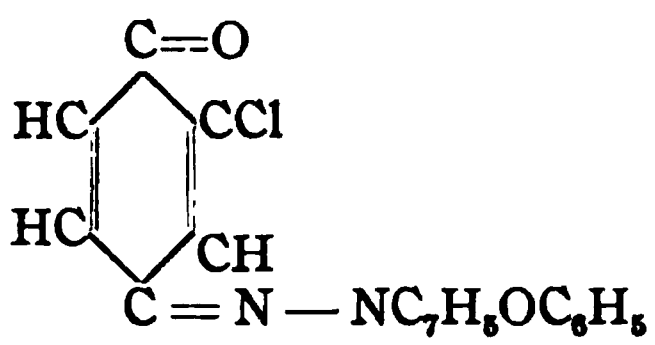
ally. As the temperature rose a yellow solid separated in the form of short, lath-shaped crystals. The mixture was set aside until it had acquired the room temperature and the solid was filtered off. A yield of 6 grams was obtained. The product was nearly pure, and after two crystallizations from benzene-ligroin melted sharply at 172.5° and gave the following results on analysis:

Calculated for $C_{19}H_{13}N_2O_2Cl$:	C, 67.72; H, 3.89; N, 8.34; Cl, 10.53.
Found:	C, 67.70; H, 4.15; N, 8.28; Cl, 10.02.

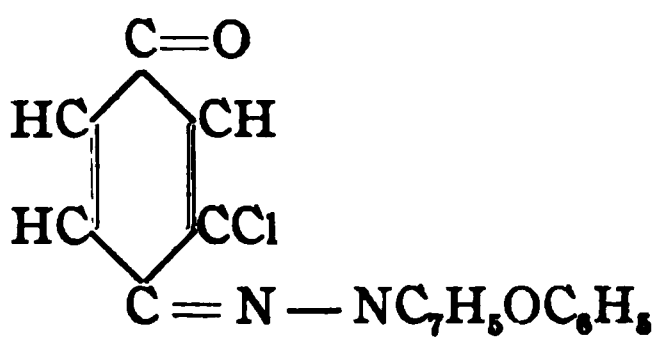
Monochlorquinonebenzoylphenylhydrazone is a yellow, crystalline compound very difficultly soluble in alcohol and ether. It readily dissolves in chloroform and benzene. From benzene it separates in rhomboids with faces almost equal in length, while from chloroform it separates in rhomboids having one axis greatly elongated. It is almost insoluble in ligroin and can best be purified by adding ligroin to a concentrated benzene solution. Phenylhydrazine acts upon it with evolution of nitrogen, although the action is not so energetic as with the corresponding non-halogenated benzoquinonehydrazone.

Action of Saponifying Agents on Monochlorquinonebenzoylphenylhydrazone.—The hydrazone was saponified by adding sulphuric acid and stirring until complete solution took place. The solution was then added slowly to water (not the reverse) when a yellow compound was formed, which collected on stirring. This was filtered, dried and purified by dissolving in ligroin. It separated from the ligroin in yellow, lath-shaped crystals, melting at 86°. The compound was soluble in sodium hydroxide and corresponded in properties to an hydroxyazo compound.

Constitution of Monochlorbenzoquinonephenylhydrazone.—In accordance with the method of preparation, the hydrazone must have one of the following formulas, depending upon whether the hydrazine condenses with the oxygen atom in the ortho or in the meta position to the chlorine.



I.



II.

It has been shown that when the corresponding non-halogenated compounds are saponified, hydroxyazo compounds are formed, the hydrogen which replaces the benzoyl group probably migrating from the nitrogen to the oxygen.

Now if formula I is correct, then on saponification one would expect to obtain benzeneazoorthochlorphenol, while if formula II is correct, then the corresponding benzeneazometachlorphenol would be formed. One

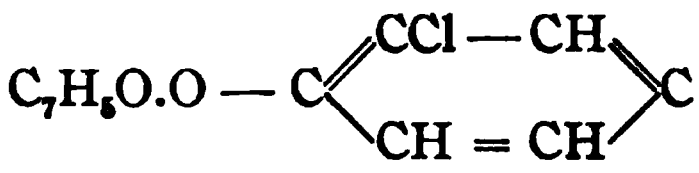
would naturally expect formula I to be the correct one, since it has been shown that hydroxylamine condenses by preference with the oxygen atom in the meta rather than in the ortho position to the chlorine. Accordingly, benzeneazoorthochlorphenol was prepared. The following method gave a good yield and a fairly pure product:

Three grams of orthochlorphenol were dissolved in a solution of 7 grams of sodium hydroxide in 100 cc. of water, and the resulting solution diluted to 1000 cc. To the cold solution was added a solution of benzene diazonium chloride made by diazotizing 3.36 grams of aniline dissolved in 15 grams of concentrated hydrochloric acid and 30 cc. of water with 2.61 grams of sodium nitrite dissolved in 20 cc. of water. The resulting solution remained clear. On neutralizing with dilute hydrochloric acid, the hydroxyazo compound separated. It was purified by repeated crystallizations from ligroin, from which it separated in from brown to yellow lath-shaped crystals.

Calculated for $C_{12}H_9N_2OCl$:	C, 61.47; H, 3.90; N, 12.07.
Found:	C, 61.20; H, 4.19; N, 12.27.

The benzeneazoorthochlorphenol so prepared is identical with the product obtained by the saponification of chlorbenzoquinonebenzoylphenylhydrazone. Each of the compounds, as well as a mixture of the two, melt at 86°. Each, when benzoylated by the Baumann reaction, give identical benzoyl derivatives, melting at 109°. Hence, formula I, given above for the hydrazone, must be the correct one.

Benzoyl Derivative of Benzeneazoorthochlorphenol,



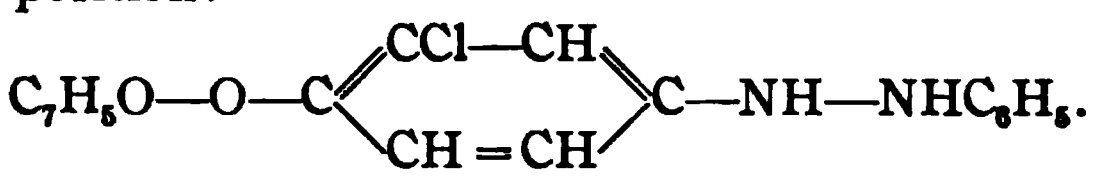
$C_7H_5O.O-C\langle{}^{CCl-CH}_{CH=CH}\rangle C-N=NC_6H_5$.—This was obtained by Baumann's reaction. After adding the benzoyl chloride, the mixture was thoroughly shaken and allowed to stand until the oily precipitate solidified. The product was easily purified by crystallization from alcohol.

Calculated for $C_{19}H_{13}N_2O_2Cl$:	C, 67.72; H, 3.89; N, 8.34.
Found:	C, 67.34; H, 3.99; N, 8.62.

Benzoylbenzeneazoorthochlorphenol is a reddish yellow compound melting at 109°. It is very soluble in hot alcohol and the solution, on cooling, becomes almost solid with a mass of curved, hair-like crystals. It is very soluble in benzene and moderately so in ether, separating from the former in clusters of feather-like crystals and from the latter in clusters of needles. It is *not identical* but *isomeric* with chlorbenzoquinonebenzoylphenylhydrazone. The hydroxyazo compound contains the benzoyl group joined to oxygen, while in the hydrazone the benzoyl group is joined to nitrogen.

Action of Reducing Agents on the Two Isomeric Benzoyl Derivatives.—The hydroxyazo compound was dissolved in acetic acid, the solution cooled

and zinc dust added; the solution at once became clear. The zinc dust was removed by filtration. On adding water to the filtrate a white precipitate was obtained, which, after purification from benzene-ligroin, melted at from 157–158°. This was dissolved in alcohol and a few drops of a solution of ferric chloride added. On standing, the original hydroxyazo compound was regenerated and separated from the alcohol in the characteristic curved, hair-like crystals. No analysis was made of the white compound obtained by the reduction, since its reactions show it to be the dihydro derivative of the original hydroxyazo compound of the following composition:



The isomeric hydrazone, when reduced in a similar way, gave an almost black solution from which, on the addition of water, a black solid separated. While this probably contained benzanilide, it was found impossible to get it sufficiently pure to determine its identity beyond any doubt.

Conversion of Monochlorquinonebenzoylphenylhydrazone into Benzoyloxyazochlorphenol.—Willstätter and Veraguth recently have described[1] a most interesting and important rearrangement of the acyl derivatives of quinonephenylhydrazones into the corresponding oxyazo compounds. By means of this reaction the chlorquinonebenzoylhydrazone described above is readily converted into the isomeric hydroxyazochlorphenol. The hydrazone was dissolved in absolute ether and heated for several hours with a small amount of anhydrous powdered potassium hydroxide, as described by Willstätter and Veraguth. The hydrazone was converted almost quantitatively into the isomeric oxyazochlorphenol, the benzoyl group migrating from the nitrogen to the oxygen.

The Action of α-Benzoylphenylhydrazine Sulphate on Monochlorquinone in a Solution of Glacial Acetic Acid. Benzeneazoorthochlorphenol Sulphate.—Two grams of α-benzoylphenylhydrazine sulphate and 5.5 grams of monochlorquinone were dissolved in separate portions of 40 cc. of glacial acetic acid. The solutions were cooled to room temperature, then mixed and slowly heated on the water-bath with occasional stirring. At about 60° a mass of dark red, silky needles separated. The mixture was set aside until cold and the crystals filtered off and dried. The resulting substance was insoluble in all the common organic solvents except hot glacial acetic acid and acetone, and only sparingly soluble in these. It was purified by washing repeatedly with hot benzene. The resulting compound melted with decomposition at 188°–190°. The properties of the compound were similar to the hydrochlorides of the hy-

[1] *Ber.*, 40, 1432.

droxyazo compounds described by Hewitt and Pope.[1] This led to the belief that it might be the sulphate of benzeneazochlorphenol. Water was poured over it, the mixture heated slightly and filtered. The resulting compound was found to be benzeneazoorthochlorphenol. The sulphuric acid in the water was determined.

Calculated for $C_{12}H_9N_2ClO.H_2SO_4$: H_2SO_4, 30.09.
Found: H_2SO_4, 29.65.

The formation of this compound is undoubtedly due to the saponification of the hydrazone at first formed, the resulting oxyazo compound then combining with the sulphuric acid originally present in the hydrazine sulphate to form the corresponding sulphate. While the hydrochlorides of a number of the hydroxyazo compounds have been prepared, so far as I know, this is the first sulphate to be described. Other quinones gave similar results, so that this method of preparation would seem to be a general one for the preparation of the sulphates of the hydroxyazo compounds.

COLUMBUS, OHIO.

STUDIES IN NITRATION. II.[2]—MELTING POINT CURVES OF BINARY MIXTURES OF ORTHO- META- AND PARANITRANILINES: A NEW METHOD FOR DETERMINING THE COMPOSITION OF SUCH MIXTURES.

BY J. BISHOP TINGLE AND H. F. ROELKER.

Received March 3, 1908.

During the last academic year the senior author, in conjunction with Dr. F. C. Blanck, carried out a somewhat extensive investigation of the nitration of *N*-substituted aniline derivatives. In the course of this work, the results of which have been awaiting publication, in the *American Chemical Journal* since the middle of August, 1907, the need was frequently felt for a simple, expeditious method for the determination of the composition of mixtures of the isomeric nitranilines. Moreover, for our purpose, it was necessary that the method should be applicable to relatively small quantities of material. The only processes of which we have been able to find descriptions in the literature consist of recrystallizations, accompanied, in some cases, by conversion of one or more of the nitranilines into some simple derivative. Apart from the question of their accuracy, such methods did not appeal to us because they certainly involve a considerable amount of labor, and probably demand for their successful operation a relatively large quantity of material.

Besides their differences in solubility, the nitranilines vary somewhat in color, in their strength as bases, and, quite widely, in their melting-

[1] *Ber.*, 30, 1624.
[2] Bishop Tingle and Blanck, *Am. Chem. J.*, 36, 605 (1906).

points. The color of the compounds, especially in dilute solutions, appeared to be too nearly alike for our purpose, and a determination of the partition of acid between the isomers involves too much trouble, consequently we decided to investigate the curves produced by plotting the melting points of binary mixtures of the nitranilines against the composition. In this connection we should like to mention that A. F. Holleman has been for some time engaged with the investigation of the influence of water on the course of nitration of benzene, acetanilide, etc., and he has also studied the influence of substitution in the benzene nucleus.[1] In the course of a paper with C. H. Sluiter[2] he gives a brief tabular statement of the melting points of a few mixtures of *p*-nitracetanilide and dinitracetanilide. In another communication, with which we were not acquainted until after our own work was in progress, he speaks of "perhaps being able to determine the composition of binary mixtures of aromatic nitro compounds by reading off from a curve the depression in the melting point of A caused by the addition of varying quantities of B." As will be seen from the contents of our paper, such a mode of procedure is inapplicable to mixtures of the nitranilines and is essentially different from the plan which we have adopted. Holleman also describes briefly and without working details, a "method of extraction," which is applicable to the determination of the composition of ternary mixtures in general.[3]

Experimental.

Materials.—The nitranilines were obtained from Kahlbaum, they melted at 71°, 114° and 147°, the temperatures given in the literature for the *o*-, *m*- and *p*-compounds, respectively. Before use they were recrystallized from 95 per cent. alcohol, in such a way that half of the substance employed remained in the mother liquor. This treatment produced no change in the melting point.

The alcohol employed in the experiments described below was the ordinary commercial 95 per cent. It was filtered before use.

Preparation of Mixtures.—A weighed quantity of each nitraniline was dissolved separately in alcohol, at the ordinary temperature; the solutions contained about 2 per cent. of ortho- and metanitraniline, respectively, but in the case of the para derivative the concentration was only about 1 per cent. The quantities of each solution required to produce a mixture of the composition desired were run out from a burette and the alcohol evaporated on the water bath. In some cases the evaporation was allowed to take place at the ordinary temperature. The residue was then placed in a desiccator on filter paper, allowed to remain

[1] *Ber.*, 39, 1715 (1906).
[2] *Rec. trav. chim.*, 26, 208 (1906).
[3] *Rep. Congres. chim. Pharm. Liege.*, p. 283, July, 1905.

about 24 hours and the melting-point determined. Fresh solutions were made up each day as required.

Orthonitraniline is very slightly volatile at the ordinary temperature and, like the other isomers, vaporizes somewhat with boiling alcohol. The magnitude of the error introduced in this manner cannot be very great, because mixtures of similar composition, prepared by evaporating the alcohol at the two temperatures mentioned, always showed the same melting point. Moreover, mixtures which had been wrapped in filter paper and exposed to the air showed no change in their melting point after several months. As will be seen from the tables, the composition of the mixtures which we employed varied by intervals of 2 per cent.

During the course of this work we had reason to suspect the accuracy of the statements made in the literature regarding the solubility of the nitranilines and we therefore made the following determinations. Separate portions of the three isomers were mixed with quantities of alcohol insufficient for complete solution, and the liquids were maintained for about 30 minutes, at 40°, in a thermostat. The clear solutions were then decanted and allowed to cool slowly to 15°. After remaining for a time at this temperature, in contact with the crystals which had separated, 10 cc. of each clear liquid was withdrawn by means of a pipette, the solutions allowed to evaporate at the ordinary temperature, and the residue dried in a desiccator. At 15°, 10 cc. of the respective solutions, in 95 per cent. alcohol, contain 1.5845 grams of ortho-, 0.4960 gram of meta- and 0.4030 gram of paranitraniline, respectively.

TABLE I.—MELTING POINT OF MIXTURES OF ORTHO- AND METANITRANILINES.

Per cent. of ortho.	M. p.	Per cent. of ortho.	M. p.	Per cent. of ortho.	M. p.	Per cent. of ortho.	M. p.	Per cent. of ortho.	M. p.
98	68.7°	78	55.3°	58	56.6°	38	57.5°	18	107.0°*
96	68.0°	76	55.0°	56	56.7°	36	60.2°	16	108.0°*
94	67.0°	74	54.8°	54	56.8°	34	58.2°	14	109.0°*
92	63.0°	72	54.6°	52	56.8°	32	57.8°	12	110.0°*
90	61.0°	70	54 0°	50	57.0°	30	57.2°	10	111.0°*
88	60.6°	68	55.4°	48	57.3°	28	64.0°	8	108.0°*
86	58.0°	66	55.6°	46	57.6°	26	70.4°	6	109.0°*
84	57.3°	64	55.7°	44	58.0°	24	80.0°	4	111.5°*
82	55.5°	62	55.8°	42	58.6°	22	87.8°	2	112.0°*
80	55.4°	60	56.5°	40	59.2°	20	104.0°		

The *melting points* were determined in the ordinary manner; the thermometer employed was a "standard" one, capable of being read to 0.1°. The temperature of the bath was usually raised rather rapidly until it was within 25° of the melting point of the substance under examination, after which the increase was about 8° per minute. No difficulty was experienced in obtaining constant results, even when the conditions were somewhat varied. In certain cases, which are duly noted, it was

found to be desirable to determine the temperature at which the substance gave *clear globules* on the sides of the melting point tubes, because for the mixtures mentioned this was much more definite than the point at which the material melted completely and collected at the bottom of the capillary. This procedure does not affect the use of the curves for quantitative purposes.

The temperatures marked * are those at which the substances melted completely (see above). These mixtures, containing from 20 to 2 per cent. of orthonitraniline, became clear and globular at temperatures higher than those required to produce the same effect in the case of specimens containing a higher proportion of ortho compound; consequently this change of standard does not invalidate the use, for analytical purposes, of the curve given below. In Fig. 1, the data contained in the above table are plotted in the form of a curve.

Fig. 1

In Table II are given the melting points of mixtures of meta- and paranitraniline.

The mixtures marked * became clear and globular (*vide* Table I) at the temperatures given, but did not melt completely. In a few cases the melting-point was not sharp, therefore we determined the limits of temperature within which the substance liquefied and give the mean value

TABLE II—MELTING POINTS OF MIXTURES OF META- AND PARANITRANILINE.

Per cent. of meta.	M. p.	Per cent. of meta.	M. p.	Per cent. of meta.	M. p.	Per cent. of meta.	M. p.	Per cent. of meta.	M. p.
98	111.5°	78	105.0°	58	91.5°	38	108.0°†	18	130.5°†
96	110.5°	76	104.5°	56	91.0°	36	111.5°†	16	135.5°†
94	111.0°	74	101.0°	54	90.5°	34	107.0°	14	136.5°
92	110.0°	72	102.0°	52	85.0°*	32	112.5°†	12	138.0°
90	107.5°	70	100.0°	50	93.0°	30	118.5°	10	140.0°
88	106.0°	68	99.0°	48	91.5°	28	123.0°†	[illegible]	142.0°
86	104.5°	66	91.0°	46	91.0	26	125.3°†	6	143.0°
84	110.5°	64	92.0°	44	98.8°†	24	122.0°	4	145.0°
82	107.0°	62	94.0°	42	95.5°	22	128.0°†	2	146.0°†
80	106.0°	60	93.5°	40	104.8°†	20	127.0°		

in the table; these figures are marked †. So far as we have been able to test the question, we have found these temperature limits to be constant. The 30 per cent. mixture was almost, but not completely, melted at 118.5°, whereas that containing 46 per cent. of meta derivative behaved exactly like a pure compound. The data in Table II are reproduced in the curve Fig. 2.

Mixtures of ortho- and paranitraniline melt in a highly irregular manner and the curve prepared from our data is quite unsuited for analytical

Fig. 2

purposes. At first we were inclined to refer this irregularity to the presence of moisture, but this is hardly probable because the pure constituents, after exposure to air, exhibit the correct melting points quite sharply; moreover, all our mixtures were treated in exactly the same manner, so that the disturbing factor should have affected each one to an equal extent. In order to make certain of this point, however, some of the mixtures were dried with very special care, but no alteration was apparent in their melting points. It may be added that of the mixtures showing the more pronounced irregularities, various specimens were prepared at different times, but the results were unchanged. The mixtures which exhibit the most marked breaks in the curve (containing 58–68 per cent. of ortho compound) do not contain the constituents in any simple molecular ratio.

At present we have no explanation to offer of the reason for the irregularities in question. It may be that they have a casual connection with the well-known simultaneous production of ortho and para disubstituted benzene derivatives and they are decidedly reminiscent of the alternate rise and fall shown in the melting point of the aliphatic monobasic acids. We are at present investigating this question more fully.

Application of the Melting Points for Analytical Purposes.

An inspection of the curves for the ortho- meta- and meta-para-mixtures shows that the direct determination of the melting point would be sufficient, within some regions of temperature, to demonstrate the composition of a substance containing either of these constituents in unknown proportion. Within a greater range of temperature, however, there are at least two mixtures of widely differing composition which have identical melting points. In such cases the determination is made as follows: Assuming that the material under examination consists of ortho- and metanitraniline, a portion of it is mixed with an approximately equal quantity of, say, pure metanitraniline, and the melting points of this mixture and of the original material are determined simultaneously, on the same thermometer. If the original material melts at a higher temperature than it does after the addition of metanitraniline, its composition is indicated by a point on the left side of the curve, otherwise by the corresponding position on the right-hand branch. If pure *orthonitraniline* is used for mixing, these relationships will be, of course, reversed. In the case of the meta-para-curve the addition of pure *paranitraniline* will *lower* the melting points of a mixture whose composition is situated to the left of the eutectic point, whereas the remaining possible mixtures, to the right of it, will have their melting points *raised* by the addition of the pure para compound. Admixture with pure *metanitraniline* will, necessarily, reverse these relations.

It will be obvious that the *quantity* of pure isomer which is added is

of no particular importance; we have found it convenient to take an amount approximately equal to that of the material under examination.

The method has been tested by the junior author, who received a number of mixtures, the composition of each of which was unknown to him. His results were accurate to 2 per cent. and in some cases agreed even more closely.

In dealing with ternary mixtures it is advisable to crystallize them fractionally from alcohol once or twice. In this manner we have found that we could obtain two portions, one containing substantially all the orthonitraniline together with some meta-, while the other portion consisted of the meta- and paraisomers. We have made a few experiments on the separation of ortho- and paranitraniline by crystallization. So far as we can judge, the separation can be made quantitatively. The mixture is weighed and treated with just sufficient boiling alcohol (95 per cent.) to dissolve it. When cool, the volume is measured. The paranitraniline which deposits is collected and to its weight is added that of the quantity dissolved in the filtrate; the sum of these, subtracted from the weight of the original material, represents the orthonitraniline.

Summary.

1. Curves have been constructed showing the relationship between the melting points and the composition of the three binary mixtures of the isomeric nitranilines.

2. In the case of the mixtures of ortho- and meta- and of meta- and paranitraniline, these curves are comparatively regular; they fall to the eutectic point and then rise to the melting point of the pure compound.

3. The curve representing the relationship between the melting point and composition of mixtures of ortho- and paranitraniline is highly irregular. At present it is impossible to give a satisfactory explanation of this phenomenon.

4. The curves mentioned above can be used to determine the composition of mixtures of otho- and meta- and of meta- and paranitraniline, respectively, by a simple and expeditious method which requires only a minimal quantity of material. The results are usually accurate within two per cent.

McMaster University,
Toronto, Canada.
December, 1907.

SOME DERIVATIVES OF 1,3-DIMETHYL-2,6-DINITROBENZENE-4-SULPHONIC ACID.

By W. J. Karslake and W. J. Morgan.

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The initial material used was the potassium salt of 1,3-dimethyl-2,6-dinitrobenzene-4-sulphonic acid, which was prepared as follows:[1] 800

[1] Claus and Schmidt, *B.* 19, 1424.

cc. commercial *m*-xylene were shaken in a separatory funnel with 800 cc. sulphuric acid, sp. gr. 1.84, for about an hour, no attempt being made to regulate the rise in temperature. After standing for an hour or so the *m*-xylenesulphonic acid solution was drawn off from the undissolved portion of the hydrocarbons and slowly added, with constant shaking, to a mixture of 1000 cc. of ordinary fuming nitric acid and 500 cc. of ordinary fuming sulphuric acid, the temperature being kept below 100°. After standing twenty-four hours, the mixture was heated to 125–130° for six or seven hours, allowed to cool, and poured into about eight liters of cold water. After filtering off the insoluble precipitate formed, which consists mostly of 2,4,6-trinitro-*m*-xylene, the filtrate was heated, neutralized with calcium carbonate, again filtered, and a hot solution of potassium carbonate added in excess. The precipitated calcium carbonate was filtered off, the filtrate evaporated to a volume of three or four liters and the potassium salt of 1,3-dimethyl-2,6-dinitrobenzene-4-sulphonic acid allowed to crystallize out. A yield of 640 grams was obtained and from the melting-point of the sulphonchloride, and sulphonamide, its identity established. It was later learned that a better yield and a purer product could be obtained by isolating the 1,3-dimethyl-6-nitrobenzene-4-sulphonic acid first formed and then nitrating this with about twice its weight of fuming nitric acid diluted with double the weight of ordinary sulphuric acid, sp. gr. 1.84.

The sulphonchloride was made in the usual manner by treating the potassium salt with an excess of phosphorus pentachloride, pouring the product into ice-water, filtering and washing, and crystallizing the residue from carbon tetrachloride. It had a melting-point of 123°.

1,3-Dimethyl-2,6-dinitrobenzene-4-sulphonanilide.—Twenty grams of aniline dissolved in 100 cc. carbon tetrachloride were added to 20 grams of the sulphonchloride previously dissolved in 200 cc. carbon tetrachloride. After heating on the water-bath for two hours in a flask connected with a return condenser the carbon tetrachloride was distilled off, the residue washed several times with dilute hydrochloric acid and afterwards with water. It was then dissolved in a ten per cent. solution of caustic potash, filtered, the filtrate acidified, with dilute hydrochloric acid, and the precipitated anilide crystallized from dilute alcohol. It separated in short, yellow needles which melted at 154°. It is easily soluble in ether or chloroform, less so in carbon tetrachloride, and insoluble in water. Upon analysis it gave 9.02 per cent. sulphur (Liebig's method) against 9.12 per cent. calculated for $C_{14}H_{13}O_6N_3S$.

1,3-Dimethyl-2,6-dinitrobenzene-4-sulphon-o-toluidide. — Five grams of the sulphonchloride dissolved in 30 cc. of carbon tetrachloride were added to four times the equivalent weight of *o*-toluidine previously dissolved in 100 cc. of carbon tetrachloride and the mixture heated in a flask with

a return condenser for four hours on the water bath. After distilling off the carbon tetrachloride the residue was treated as in the preparation of the anilide. From ninety-five per cent. alcohol the *o*-toluidide separated in white radiating nodules, while from a mixture of benzene and alcohol it crystallized in white needles. It had a melting-point of 135°. Upon analysis it gave 8.68 per cent. sulphur against 8.76 per cent. required for $C_{15}H_{15}O_6N_3S$.

1,3-Dimethyl-2,6-dinitrobenzene-4-sulphon-p-toluidide.—Three times the equivalent weight of *p*-toluidine was heated with 5 grams of the sulphonchloride in the presence of dilute caustic potash for about half an hour on the water-bath. The mixture was then filtered and the filtrate acidified with dilute hydrochloric acid until no further precipitation took place. The *p*-toluidide so obtained was crystallized from alcohol and separated in yellow plates or in silky needles having a melting-point of 162°. It is soluble in chloroform, less so in carbon tetrachloride, and insoluble in water. Upon analysis it gave 8.96 per cent. sulphur against 8.76 required by theory.

1,3-Dimethyl-2,6-dinitrobenzene-sulphone-benzene.—Five grams of the sulphonchloride were dissolved in an excess of benzene and one gram of anhydrous aluminum chloride added. The mixture was then heated for three hours in a flask with a reflux condenser on the water-bath. The excess of benzene was distilled off and the residue successively treated with dilute caustic soda solution, dilute hydrochloric acid and water, and then dried. It was finally digested with carbon tetrachloride and a small quantity of boneblack, filtered, and allowed to cool. The sulphone separated in large glistening plates, which melted at 178°. Upon analysis it gave 9.70 per cent. sulphur against 9.52 per cent. required for $C_{14}H_{12}O_6N_2S$.

1-Carboxy-3-methyl-2,6-dinitrobenzene-4-sulphonic Acid(?).—Eight hundred grams of the potassium salt of 1,3-dimethyl-2,6-dinitrobenzene-4-sulphonic acid were dissolved at room temperature in five liters of water and to it was added a solution of 1700 grams of potassium permanganate, 50 grams of caustic potash, and enough water to dilute the whole to 120 liters. After standing three weeks at room temperature the solution was warmed on the water-bath, decolorized by the addition of a little alcohol, filtered from the manganese dioxide, and evaporated to crystallization. One hundred grams of unchanged original potassium salt separated out. This was filtered off, the filtrate acidified with hydrochloric acid, evaporated to dryness, and extracted with alcohol. The alcoholic solution upon evaporation to dryness gave a sirupy liquid which was treated with phosphorus pentachloride, poured into ice-water, the insoluble residue thoroughly washed with water and, after drying, crystallized from carbon tetrachloride. The crystals thus obtained were brown in

color, granular, and irregular in shape. They melted at 127–128° and were probably an impure acid chloride. Upon digestion with concentrated aqueous ammonia they formed a product which, upon crystallization from alcohol, gave yellow plates possessing no definite melting-point and charring at about 290°. They were not analyzed. The residue, which was insoluble in alcohol, was recrystallized several times from water and then analyzed. The results obtained indicate that one of the two methyl groups, CH_3, present in the original salt, was oxidized to the corresponding carboxyl group, CO.OH, but it yet remains to be shown which one of them it was. We are hoping to determine this point in the near future. Tentatively it is assumed to be that methyl group which is in the first position (1). Upon this assumption the salt obtained was the acid potassium salt of 1-carboxy-3-methyl-2,6-dinitrobenzene-4-sulphonic acid and contains one molecule of water of crystallization. The analysis gave 11.04 per cent. potassium, 5.00 per cent. water, 9.00 per cent. sulphur, against 11.08 per cent. potassium, 4.97 per cent. water, 8.83 per cent. sulphur required by theory.

The *acid barium salt* was obtained by adding barium carbonate to the hot solution of the acid potassium salt, filtering, and adding hydrochloric acid to the filtrate. Upon coooling there separated yellow plates containing three molecules of water of crystallization. The analysis gave 15.59 per cent. barium, 12.68 per cent. water, compared to 16.06 per cent. barium, 12.62 per cent. water calculated according to theory.

The *neutral barium salt* was prepared by adding barium carbonate to the hot solution of the acid potassium salt and filtering. It separated in light yellow plates containing no water of crystallization. The analysis gave 30.98 per cent. barium against 30.90 per cent. barium required by theory.

The *neutral strontium salt* was formed by adding strontium carbonate to the hot solution of the acid potassium salt and filtering. It separated in almost white, square crystals containing no water of crystallization. The analysis gave 21.81 per cent. strontium against 22.08 per cent. required by theory.

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CONCERNING α-DINAPHTHYL SELENIDE AND TELLURIDE.

BY R. E. LYONS AND G. C. BUSH.

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Some years ago, while collecting and tabulating material for the comparative study of the periodic relationship in the oxygen family, especially in the organic combinations of sulphur, selenium and tellurium, we were led to undertake the synthesis of certain aromatic compounds of

selenium and tellurium necessary to fill in the blank spaces in the chart. The work was not completed because of our separation. The compounds prepared in this connection are as yet unreported and may be described as follows:

1. *α-Dinaphthyl Selenide*, $(C_{10}H_7)_2Se$. — Krafft and Lyons[1] prepared phenyl telluride by heating together mercury diphenyl and metallic tellurium. We undertook the preparation of α-dinaphthyl selenide in an analogous manner from α-dinaphthyl mercury and selenium:

$$(C_{10}H_7)_2Hg + 2Se = HgSe + (C_{10}H_7)_2Se.$$

A mixture of 4.5 grams α-dinaphthyl mercury, m. p. 242°, and 1.58 grams finely powdered selenium, contained in a small Anschütz flask, was kept in a Wood's metal bath at 190° under a pressure of 16 mm. for about 12 hours. A temperature above 200° was found unfavorable, causing the dinaphthyl mercury to split into mercury and naphthalene. When cool, the mixture was distilled with steam to remove the naphthalene and the residue extracted with ether. Evaporation of the extracts gave 1.7 grams, or 54 per cent. of the theoretical amount of the dinaphthyl selenide. The product crystallized from absolute alcohol, in which it is moderately soluble, in fine, faintly yellow, glittering leaflets, which melted at 114°. Neither treatment with charcoal nor crystallization from other solvents, as ether or amyl alcohol, gave a colorless product. Exposure to air and light effects rapid decomposition of the selenide.[2]

$(C_{10}H_7)_2Se$, Calculated: C, 72.28; H, 4.18.
Found: C, 72.20; H, 4.11.

The selenium in the compound was determined by the method of Lyons and Shinn.[3] 0.3816 gram required 45.7 cc. $N/10$ sodium thiosulphate. Calculated, 23.73; found, 23.65 per cent. Se.

2. *α-Dinaphthyl Selenide Dibromide*, $(C_{10}H_7)_2Se.Br_2$.—When the theoretical quantity of bromine was slowly added to a warm alcoholic solution of the selenide and the mixture allowed to stand for several hours the dinaphthyl selenide dibromide separated out in the form of dirty white needles. The yield was practically quantitative. The bromide is soluble in amyl alcohol, but was more readily crystallized from carbon disulphide as white, delicate needles which melted at 183° with decomposition.

Calculated for $(C_{10}H_7)_2Se.Br_2$: Br, 32.45.
Found: Br, 32.31.

Diphenyl selenium oxide[4] and diphenyl tellurium oxide[5] have been ob-

[1] *Ber.*, **27**, 1769.

[2] All selenium and tellurium compounds described in this paper are so affected in varying degrees.

[3] THIS JOURNAL, **24**, 1087.

[4] *Ber.*, **26**, 2819.

[5] *Ibid.*, **27**, 1770.

tained by treating the respective bromides with dilute solutions of sodium hydroxide. The treatment of α-dinaphthyl selenide dibromide with solutions of sodium hydroxide of varying concentration at different temperatures failed to produce the desired dinaphthyl selenium oxide, $(C_{10}H_7)_2SeO$. Boiling with 15 per cent. sodium hydroxide solution produced no change in the substance. A 25 per cent. solution of the alkali was without action at room temperature, but at about 90° the bromine was removed. That oxygen did not take its place was shown by the recovery of dinaphthyl selenide from the reaction mixture.

3. *α-Dinaphthyl Selenide Dichloride*, $(C_{10}H_7)_2Se.Cl_2$.—A current of dry chlorine gas passed into an ether solution of the dinaphthyl selenide produced immediately a heavy, white, amorphous precipitate of dinaphthyl selenide dichloride. The chloride is insoluble in alcohol, ether, chloroform, benzene, ligroin, carbon disulphide and amyl alcohol; easily soluble in xylene, from which it crystallizes in colorless prisms melting at 130°.

Calculated for $(C_{10}H_7)_2Se.Cl_2$: Cl, 17.53.
Found: Cl, 17.40.

4. *α-Dinaphthyl Telluride*, $(C_{10}H_7)_2Te$.—This compound was obtained by heating together molecular quantities of α-dinaphthyl mercury and tellurium according to the method successfully used in the preparation of phenyl telluride and α-dinaphthyl selenide,

$$(C_{10}H_7)_2Hg + 2Te = HgTe + (C_{10}H_7)_2Te.$$

A mixture of 4.5 grams dinaphthyl mercury and 2.5 grams powdered tellurium, contained in a small Anschütz flask, attached to a vacuum pump, was kept at 190–198° and 16.5 mm. pressure for about 8 hours. After cooling, the solidified mass was distilled with steam to effect the removal of the naphthalene which had collected in the upper portion of the flask. The residue was then extracted with ether, the ether solution quickly filtered and evaporated, to avoid excessive separation of tellurium. The solid residue was purified by crystallization from much alcohol. Three crystallizations of the telluride from alcohol gave glittering brownish yellow leaflets which melted at 126.5°. The yield of the crude product was 53 per cent. of the theoretical. Excessive or prolonged heating of the reaction mixture brings about a secondary change resulting in the formation of a yellow product which melts at about 190° and imparts to alcohol, ether, carbon disulphide and other solvents a very pronounced fluorescence. The product was tellurium-free and was not further examined.

$(C_{10}H_7)_2Te$, Calculated: C, 63.33; H, 3.69.
Found: C, 63.23; H, 3.49.

The tellurium was determined by decomposition of the substance with red fuming nitric acid in a Carius tube, reducing the tellurous acid in

hydrochloric acid solution with sodium bisulphite, collecting the precipitate on a weighed Gooch filter, drying at 105°, and weighing.

Calculated for $(C_{10}H_7)_2Te$: Te, 32.98.
Found: Te, 32.79.

5. *α-Dinaphthyl Telluride Dibromide*, $(C_{10}H_7)_2Te.Br_2$.—The addition of bromine to an ether or alcoholic solution of α-dinaphthyl telluride gave immediately a heavy yellow precipitate of dinaphthyl telluride dibromide. The precipitate was washed with ether and crystallized from carbon disulphide, in which it is sparingly soluble, as sparkling, lemon-yellow granules, which melted with decomposition at 244°. If the bromine is added to an exceedingly dilute, warm, alcoholic solution of the telluride and the mixture be allowed to stand for several hours, fine yellow crystals of the bromide separate, which, after washing and drying, melt at 244°.

Calculated for $(C_{10}H_7)_2Te.Br_2$: Br, 29.57.
Found: Br, 29.67.

6. *α-Dinaphthyl Telluride Dichloride*, $(C_{10}H_7)_2Te.Cl_2$.—When a current of dry chlorine is passed into an ether solution of α-dinaphthyl telluride a heavy white precipitate of the chloride is formed. The chloride is insoluble in all of the ordinary solvents, but is sparingly soluble in xylene, from which it crystallizes in glittering, colorless granules, melting at 265°.

Calculated for $(C_{10}H_7)_2Te.Cl_2$: Cl, 15.74.
Found: Cl, 15.83.

7. *Diphenyl Telluride Dichloride*, $(C_6H_5)_2Te.Cl_2$, was prepared by passing dry chlorine gas into an ether solution of diphenyl telluride[1] and purified by recrystallization from xylene, in which it is very readily soluble. Long, white prisms, melting at 160°.

Calculated for $(C_6H_5)_2Te.Cl_2$: Cl, 20.24.
Found: Cl, 20.36.

8. *β-Dinaphthyl Selenide Dichloride*, $(C_{10}H_7)_2Se.Cl_2$, was prepared by the action of dry chlorine gas upon the selenide in ether solution. By recrystallization from carbon disulphide it was obtained in almost colorless leaflets, melting at 146°.

Calculated for $(C_{10}H_7)_2Se.Cl_2$: Cl, 17.53.
Found: Cl, 17.60.

From the time of Doebereiner the similarity of sulphur, selenium and tellurium compounds has been a subject of comment. There is, in general, a pronounced similarity in methods of formation, in deportment and in the effect of substituents in the compounds of these elements with organic radicals. The changes in the physical constants, *e. g.*, boiling-point, melting-point, to be observed in a comparison of sulphides, selenides

[1] *Ber.*, 27, 1769.
[2] *Ibid.*, 27, 1767.

and tellurides of like radicals, are usually gradual and progressive with the increase in magnitude of the atomic weights. Data concerning the compounds described in this paper and some related compounds, previously reported,[1] are placed in the following tables:

Sulphides.	B. p. (16 mm.).	Selenides.	B. p. (16 mm.).	Tellurides.	B. p. (16 mm.).
$(C_6H_5)_2S$	157°	$(C_6H_5)_2Se$	167°	$(C_6H_5)_2Te$	182°
$C_6H_5.SH$	172°	$C_6H_5.SeH$	183°	.....	....
	M. p.		M. p.		M. p.
$(C_6H_5)_2S.S$	60°	$(C_6H_5)_2Se.Se$	63.5°	.....	....
$(C_6H_5)_2SO$	70.5°	$(C_6N_5)_2SeO$	114°	$(C_6H_5)_2TeO$	187°
α-$(C_{10}H_7)_2S$	110°	α-$(C_{10}H_7)_2Se$	114°	α-$(C_{10}H_7)_2Te$	126.5°
β-$(C_{10}H_7)_2S$	151°	β-$(C_{10}H_7)_2Se$	138.5°	.....	....
$(o$-$CH_3.C_6H_4)_2S$	64°	$(o$-$CH_3.C_6H_4)_2Se$	62°	$(o$-$CH_3.C_6H_4)_2Te$	38°
$(p$-$CH_3.C_6H_4)_2S$	57°	$(p$-$CH_3.C_6H_4)_2Se$	69°	$(p$-$CH_3.C_6H_4)_2Te$	64°
$(C_6H_4Cl)_2S$	88°	$(C_6H_4Cl)_2Se$	96°	.....	....
$(C_6H_4Br)_2S$	109.5°	$(C_6H_4Br)_2Se$	115.5°	.....	....

THE HALOGEN ADDITION PRODUCTS.

Chlorides.	M. p.	Bromides.	M. p.
$(C_6H_5)_2S.Cl_2$	....	$(C_6H_5)_2S.Br_2$	....
$(C_6H_5)_2Se.Cl_2$	183°	$(C_6H_5)_2Se.Br_2$	148°
$(C_6H_5)_2Te.Cl_2$	160°	$(C_6H_5)_2Te.Br_2$	203°
β-$(C_{10}H_7)_2S.Cl_2$	....	β-$(C_{10}H_7)_2S.Br_2$	....
β-$(C_{10}H_7)_2Se.Cl_2$	146°	β-$(C_{10}H_7)_2Se.Br_2$	161°
β-$(C_{10}H_7)_2Te.Cl_2$	....	β-$(C_{10}H_7)_2Te.Br_2$	....
α-$(C_{10}H_7)_2S.Cl_2$	....	α-$(C_{10}H_7)_2S.Br_2$	....
α-$(C_{10}H_7)_2Se.Cl_2$	130°	α-$(C_{10}H_7)_2Se.Br_2$	183°
α-$(C_{10}H_7)_2Te.Cl_2$	265°	α-$(C_{10}H_7)_2Te.Br_2$	244°
$(p$-$CH_3.C_6H_4)_2S.Cl_2$	....	$(p$-$CH_3.C_6H_4)_2S.Br_2$	....
$(p$-$CH_3.C_6H_4)_2Se.Cl_2$	177°	$(p$-$CH_3.C_6H_4)_2Se.Br_2$	162°
p-$CH_3.C_6H_4)_2Te.Cl_2$	....	$(p$-$CH_3.C_6H_4)_2Te.Br_2$	201°
$(o$-$CH_3.C_6H_4)_2Se.Cl_2$	152°	$(o$-$CH_3.C_6H_4)_2SeBr_2$	84°
$(o$-$CH_3.C_6H_4)_2Te.Cl_2$	....	$(o$-$CH_3.C_6H_4)_2Te.Br_2$	182°

Consideration of the rather limited number of these compounds now available shows that the change in boiling and melting point generally, but not always, varies directly with the magnitude of the atomic weight. The first known and simpler compounds of these elements, *e. g.*, the phenyl compounds, conform to this and exhibit differences which are strikingly constant. However, examination of all of the data given in the above tables shows that the change does not follow a rigid or fixed rule. In some instances the changes are very abrupt and out of proportion to the difference between the atomic weights; in other instances the change is the reverse of the expectation and is without plausible explanation, *e. g.*, *o*-tolyl sulphide, selenide and telluride show the melting-points 64°, 62° and 38°, respectively. The melting-point decreases as the atomic weight increases and the drop from 62° to 38° is abrupt.

[1] *Ber.*, **26**, 2818; **27**, 1764; **28**, 1670.

The changes are even more erratic and irregular in the halogen addition products. An extreme case is found in the *o*-tolyl selenide dichloride and dibromide melting at 152° and 84°, respectively. The halogen substitution products, thus far reported, exhibit differences which are more nearly constant than is observed among the halogen addition products.

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March, 1908.

(CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.)

HYDRAZONES OF AROMATIC HYDROXYKETONES. ALKALI-INSOLUBLE PHENOLS.

SECOND PAPER.

BY HENRY A. TORREY AND H. B. KIPPER.

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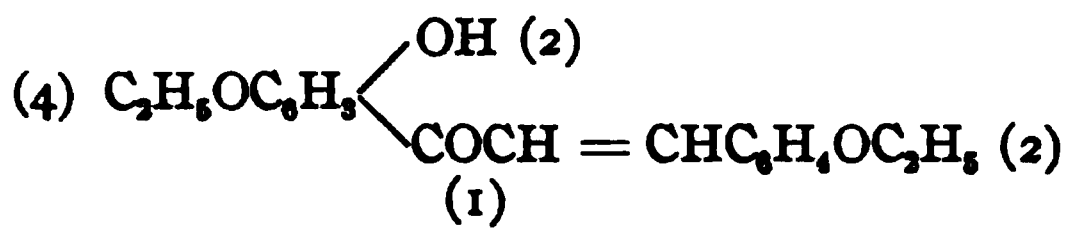
Although it is a very general rule, so general indeed that it is almost universal, that phenols are soluble in aqueous alkalies, there are certain substances of this class that are marked exceptions. The work described in this paper consists of an extension of the list of such compounds, and some investigation of the conditions to which this alkali-insolubility is due. While studying the phenylhydrazones of certain hydroxy aceto- and benzophenones, it was found, as mentioned in an earlier paper,[1] that when the free hydroxyl was in the ortho position with reference to the substituted ketone group, the substance was insoluble in strong aqueous alkalies. Substances showing this characteristic property have been obtained and studied by others. O. Anselmino[2] studied the phenylhydrazones of homosalicylaldehydes and obtained alkali-insoluble compounds similar to ours. Liebermann[3] first discussed in detail the alkaline insolubility of benzene azonaphthol, which was later studied by Goldschmidt and R. Brubacher,[4] McPherson[5] and Hantzsch and Farmer.[6] St. v. Kostanecki has obtained certain nitrogen-free phenols which are insoluble in alkalies; thus A. Cornelson and St. v. Kostanecki[7] report that 2-hydroxy-benzaldiacetophenone,

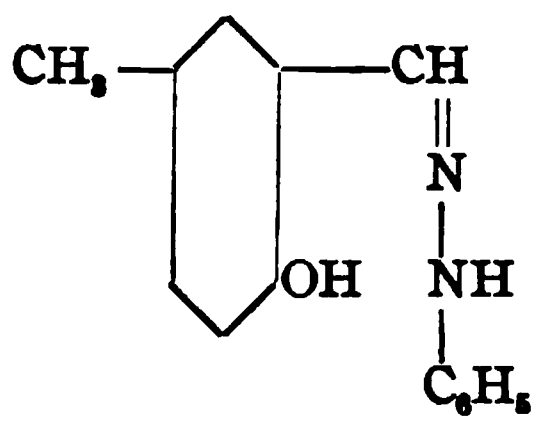
$$HOC_6H_4CH(CH_2COC_6H_5)_2,$$

is insoluble in warm dilute sodium hydroxide, although it does dissolve in hot 15 per cent. potassium hydroxide, and St. v. Kostanecki and R. v. Salis[8] state that 2-ethoxybenzalresacetophenonmonoethyl ether,

[1] THIS JOURNAL, 29, 77.
[2] *Ber.*, 35, 4099.
[3] *Ibid.*, 16, 2858.
[4] *Ibid.*, 24, 2306.
[5] *Ibid.*, 28, 2418.
[6] *Ibid.*, 32, 3100.
[7] *Ibid.*, 29, 242.
[8] *Ibid.*, 32, 1030.



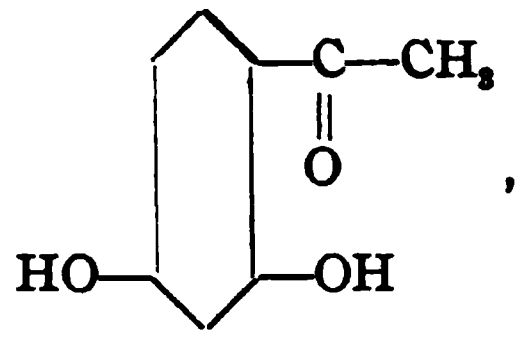
is insoluble in aqueous alkalies. Rogow[1] and R. Fosse and A. Robyn,[2] by the condensation of hydroxyaldehydes with β-naphthol, obtained dinaphthoxanthenes, containing hydroxyl groups, which were insoluble in aqueous sodium hydroxide. Rogow[1] mentions also condensation products of hydroxy-aldehydes with β-naphthylamine which are almost insoluble in dilute alkalies. The phenylhydrazone of *p*-homosalicylaldehyde, as obtained by Anselmino, is a compound entirely insoluble in cold, highly concentrated alkalies. The phenylhydrazone of salicyl-



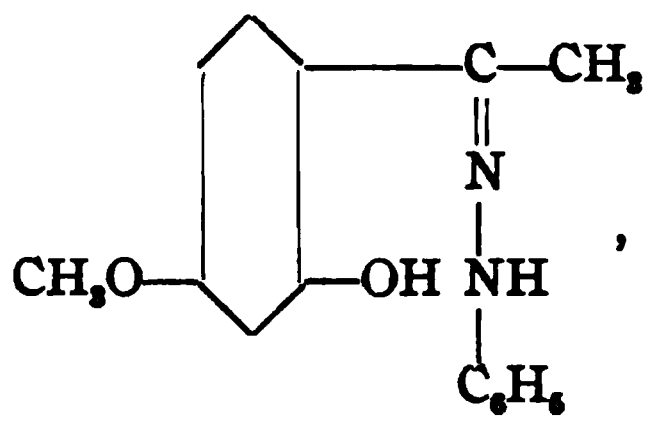
aldehyde, on the other hand, although its hydroxyl group is in the ortho position to the side chain carrying the hydrazone radical, is, nevertheless, soluble in alkalies. The solubility of the phenol is therefore influenced by the presence of the methyl group, and this effect is even more marked when more than one methyl group is present. Anselmino prepared a number of derivatives of this nature, including in addition to the phenylhydrazones, azines and semicarbazones. Those phenoxyaldehydes, however, which gave phenylhydrazones, insoluble in aqueous sodium hydroxide, gave azines and semicarbazones which were soluble in this reagent. He found also that phenylhydrazones of all *para*-hydroxyaldehydes were normally reacting phenols, dissolving easily in alkalies of all concentrations, and being reprecipitated with acids. Our investigation of the phenylhydrazones of the *o*-hydroxy-, aceto- and benzophenones was begun with the idea of obtaining a product of a secondary condensation between the hydroxyl group and the imide group, and the alkali-insolubility of many of the phenylhydrazones which we obtained lent color to the belief that such a condensation had actually occurred. The analytical results and the subsequent work, however, made such a conclusion untenable. We have already mentioned the influence of the methyl groups on the alkali-insolubility of the derivatives of the aldehydes, as studied by Anselmino; in none of the compounds which we have investigated is there an alkyl group directly attached to the ring, but we have found that the presence of other groups in the ring has the same

[1] *Ber.*, **33**, 3535; *J. pr. Ch.* [2], **72**, 320.
[2] *Compt. rend.*, **132**, 789; **137**, 858; **138**, 2820; **140**, 1538.

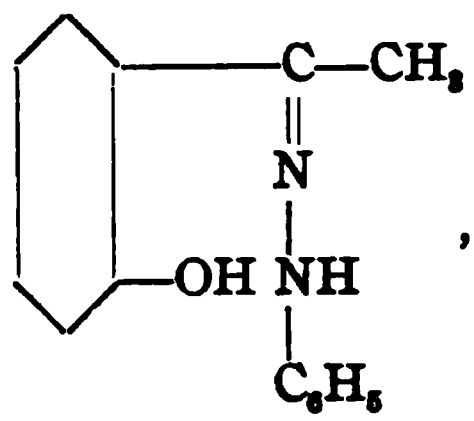
influence. Our work has been directed chiefly toward the study of phenylhydrazones and other similar derivatives of resacetophenone and resodiacetophenone. In resacetophenone,



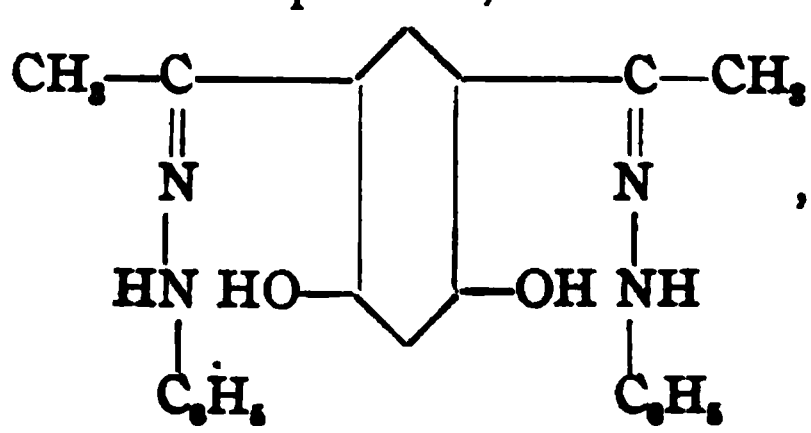
one hydroxyl group is ortho and the other para to the ketone side chain and its phenylhydrazone is, as would be expected, easily soluble in alkalies. The phenylhydrazone of paeonol,



however, in which the only free hydroxyl is ortho to the large side chain, is insoluble in aqueous alkalies, although paeonol itself is readily soluble. Since the phenylhydrazone of *o*-hydroxyacetophenone,



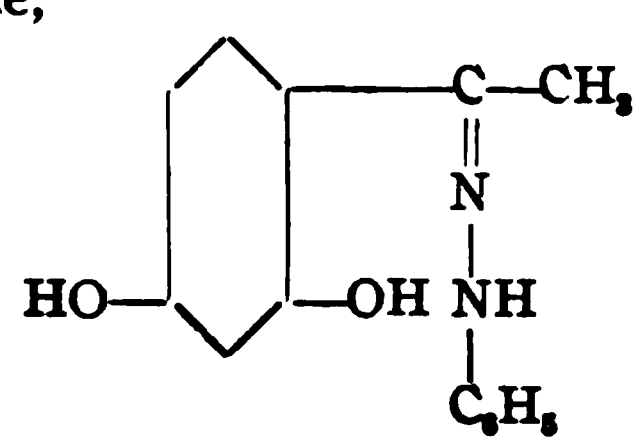
is soluble in alkalies, it is evident that the methoxy group in paeonol has a real influence upon the solubility. We have found also that the C_6H_5COO—, the $CH_3C{=}NNHC_6H_5$, and the $C_6H_5C{=}N.NHC_6H_5$ groups are contributing factors in this phenomenon of alkaline insolubility. To make clearer the influence of these last two groups upon the solubility, it is only necessary to call to notice the fact that although the phenylhydrazone of *o*-hydroxyacetophenone, whose formula has just been given, is soluble, the bisphenylhydrazone of resodiacetophenone,



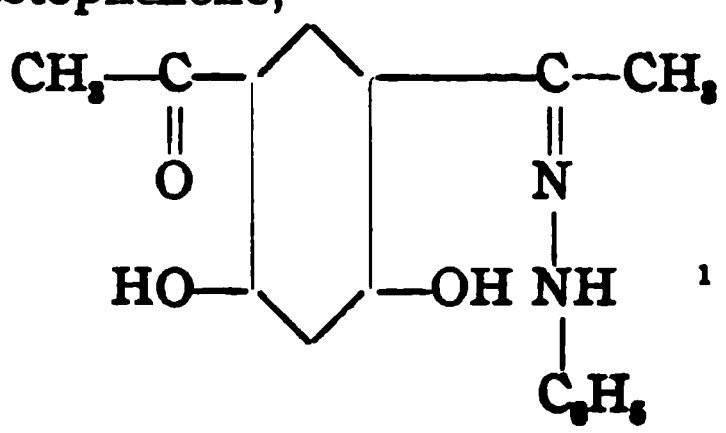
is exceedingly insoluble, even in hot aqueous alkalies. Thus, if we consider the influence of the substituting groups upon one hydroxyl at a time, we may say that the insolubility is brought about by the joint influence of the $CH_3\overset{|}{C}=N—NHC_6H_5$ adjacent to the given hydroxyl and of the other $CH_3\overset{|}{C}=N—NHC_6H_5$, this second group playing the part of the methoxy group in paeonol or the methyl groups in the aldehyde derivatives. While the benzidine derivative of resodiacetophenone, in which two molecules of benzidine have condensed with two molecules of the ketone, shows the same insolubility toward alkalies as the phenylhydrazone, the azine and semicarbazones are soluble. If we tabulate the phenols that we have studied according to their solubility in aqueous alkalies, they fall into the following groups:

Soluble in Aqueous Alkalies.

Phenylhydrazone of resacetophenone,

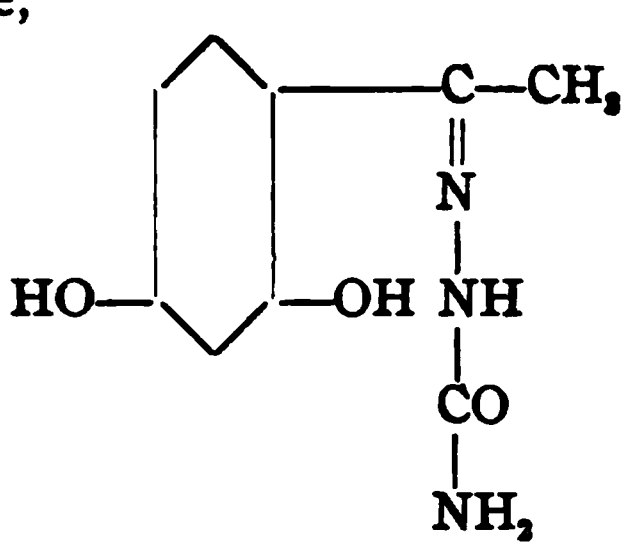


Monophenylhydrazone of resodiacetophenone,

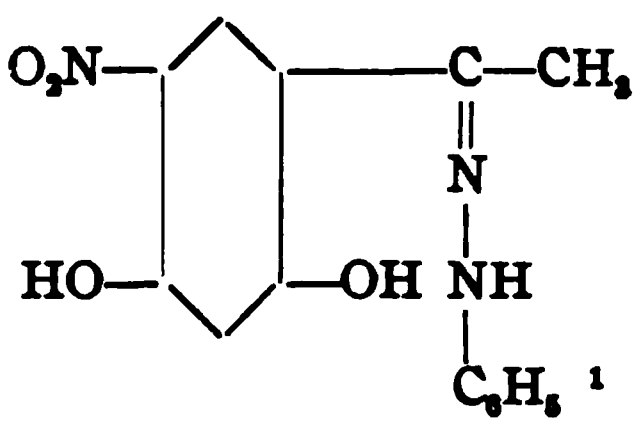


[1]

Semicarbazone of resacetophenone,

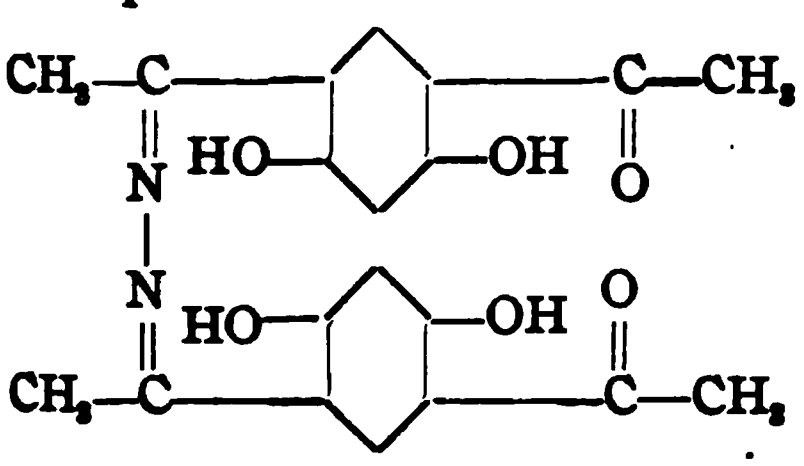


Phenylhydrazone of nitroresacetophenone,

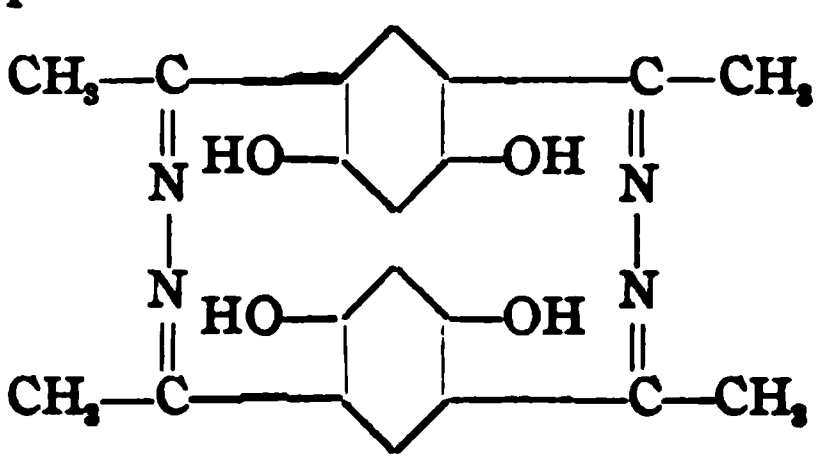


[1]

Monoazine derivative of resodiacetophenone.



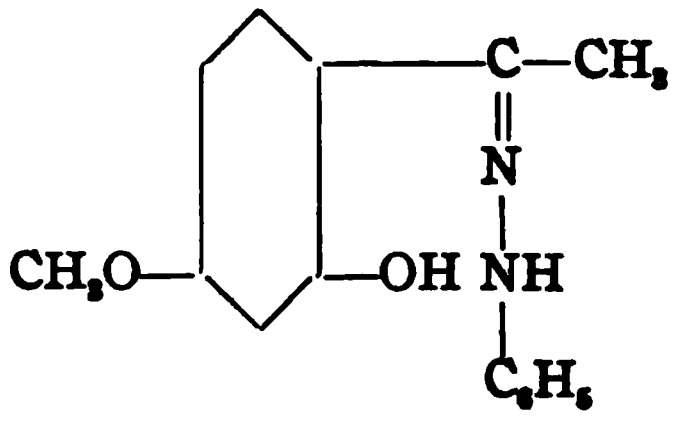
Bisazine derivative of resodiacetophenone.



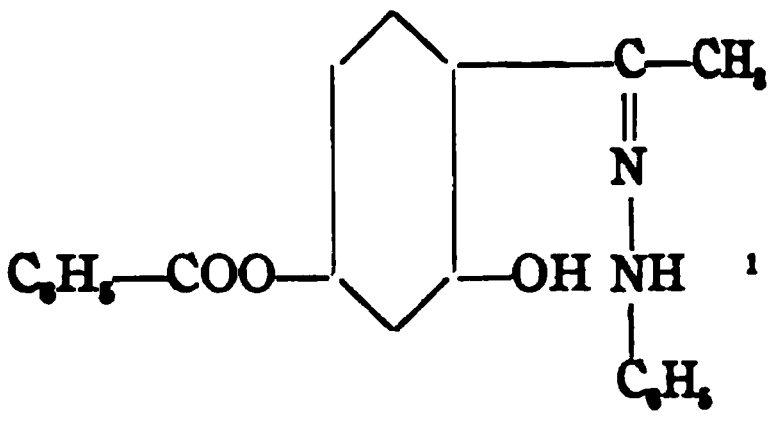
[1] Position of nitro group not proved.

Insoluble in Aqueous Alkalies.

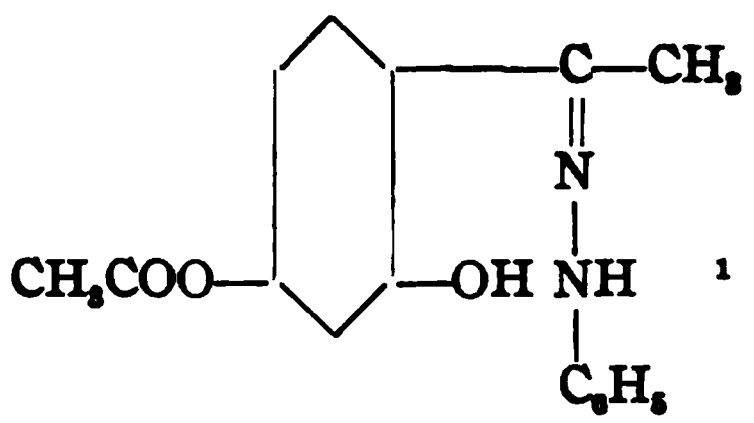
Phenylhydrazone of paeonol,



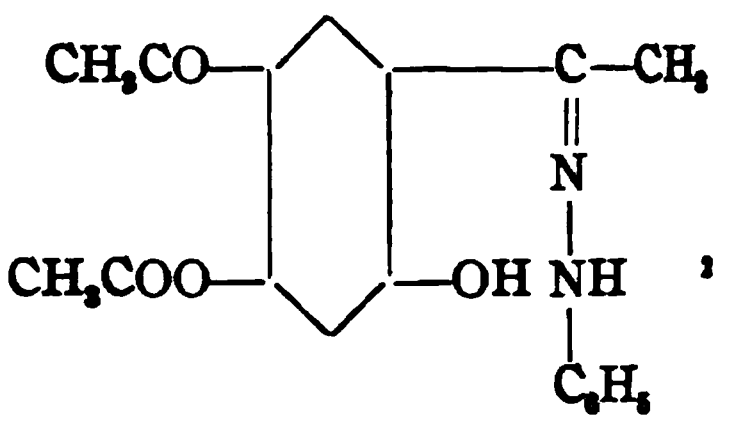
Phenylhydrazone of resacetophenone-4-monobenzoate,



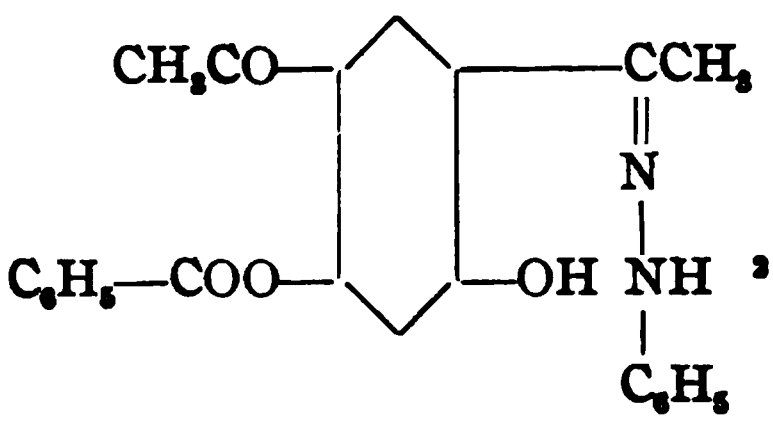
Phenylhydrazone of resacetophenone-4-monoacetate,



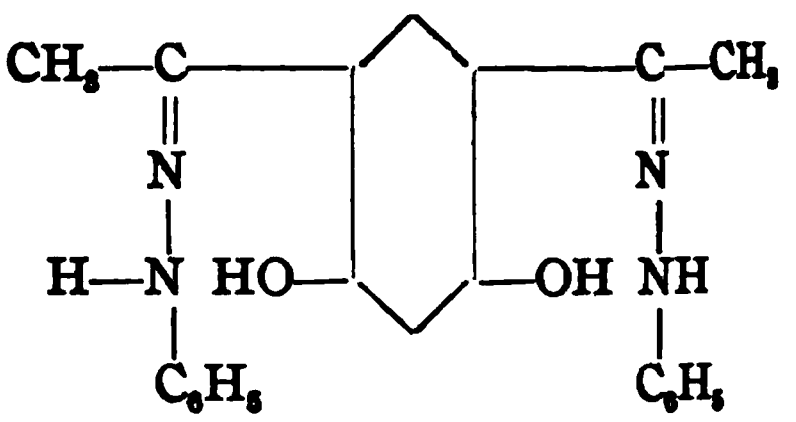
Phenylhydrazone of resodiacetophenone monacetate,



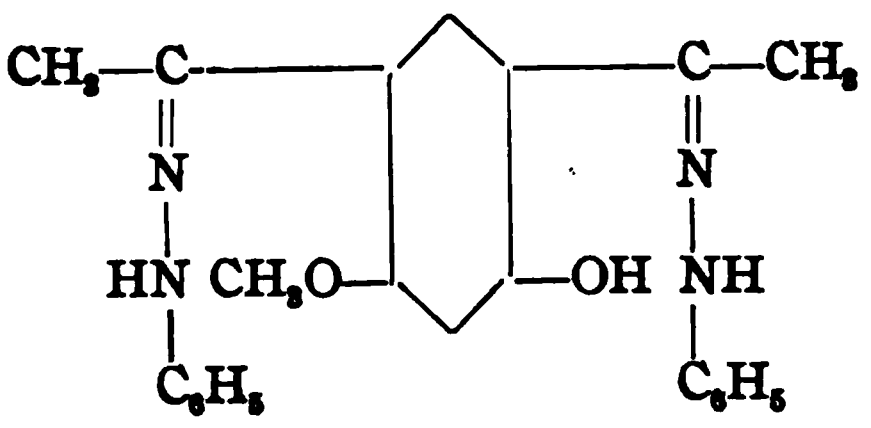
Phenylhydrazone of resodiacetophenone monobenzoate,



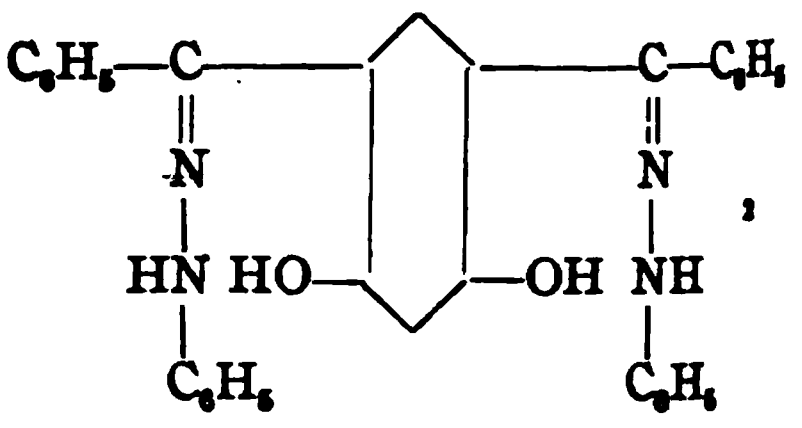
Bisphenylhydrazone of resodiacetophenone,



Bisphenylhydrazone of monomethyl ether of resodiacetophenone,

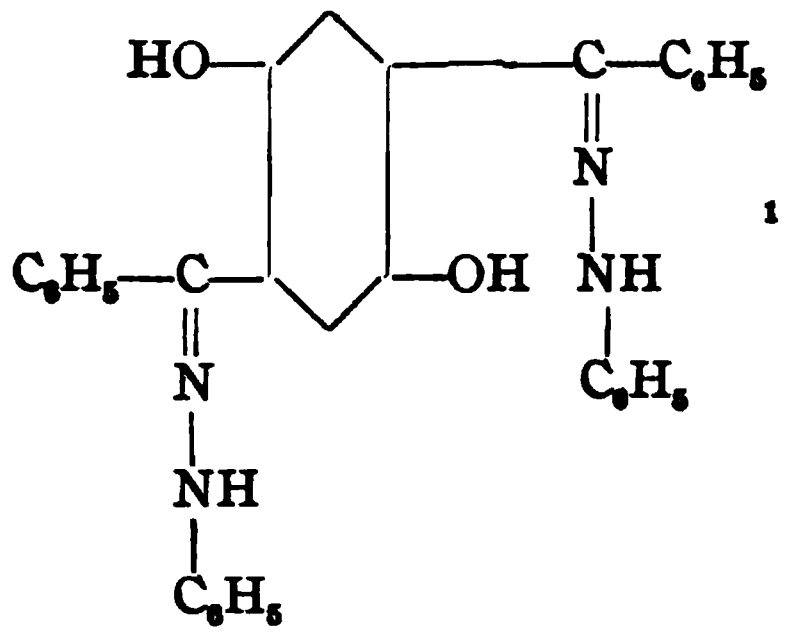


Bisphenylhydrazone of dibenzoresorcinol,



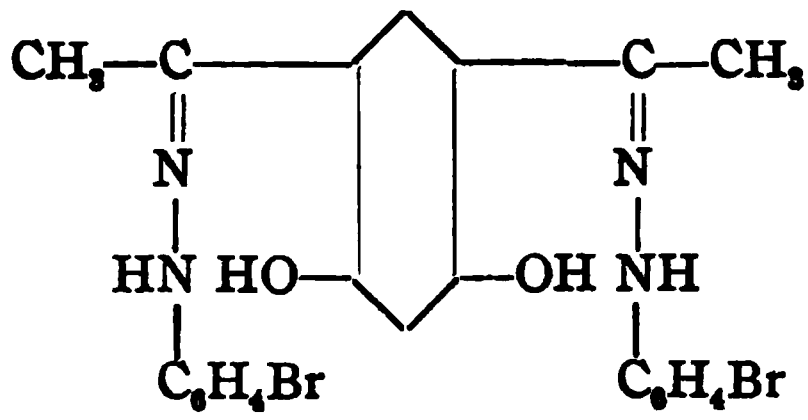
[1] Position of Br not proved.
[2] Saponified by alkalies.

Bisphenylhydrazone of dibenzohydroquinonol,

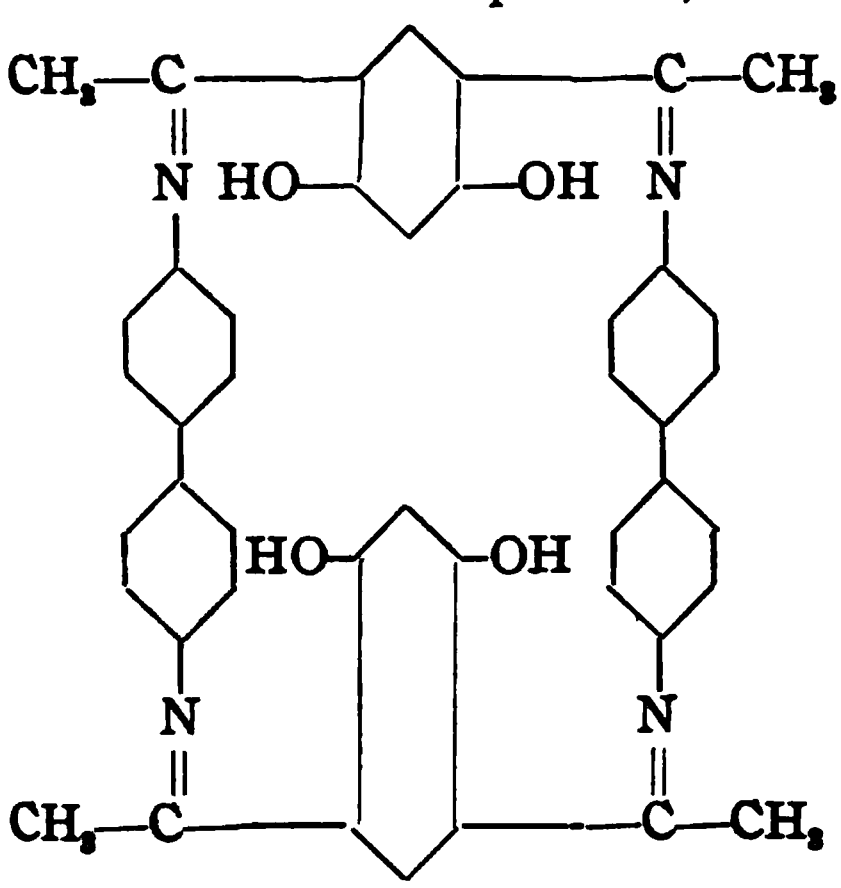


[1]

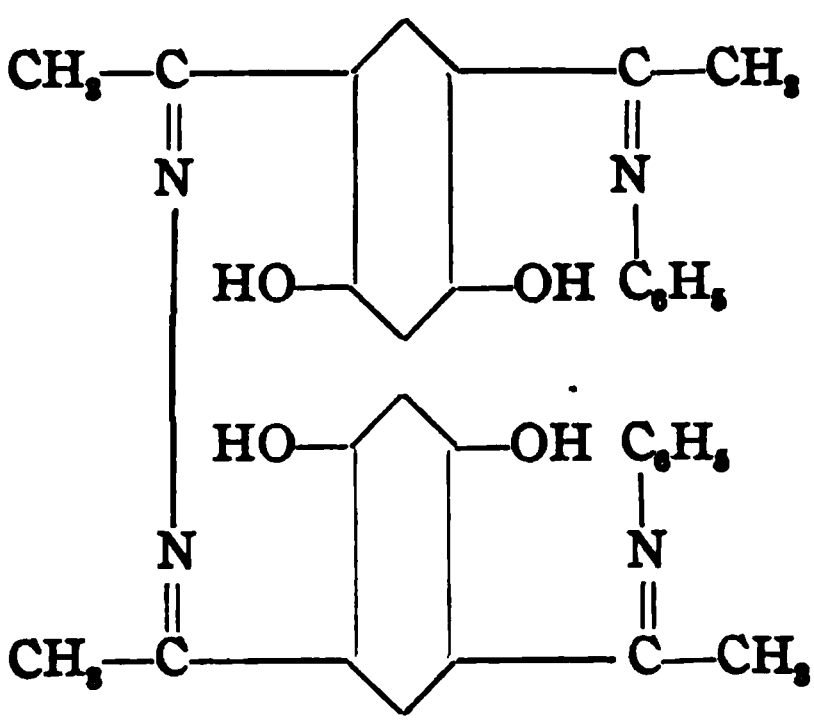
Bis *p*-bromphenylhydrazone of resodiacetophenone,



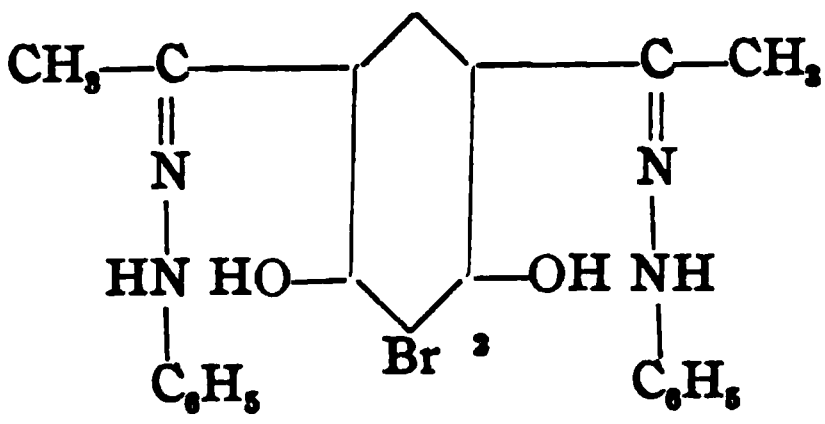
Condensation product of benzidine and resodiacetophenone,



Dianilido monazine derivative of resodiacetophenone,



Bisphenylhydrazone of monobromresodiacetophenone,



[2]

It will be noticed that in the compounds that we have studied, the insolubility in aqueous alkalies is determined by the *two* following conditions: (1) The free hydroxyl group is ortho to a large side chain, as

[1] THIS JOURNAL, 29, 81.

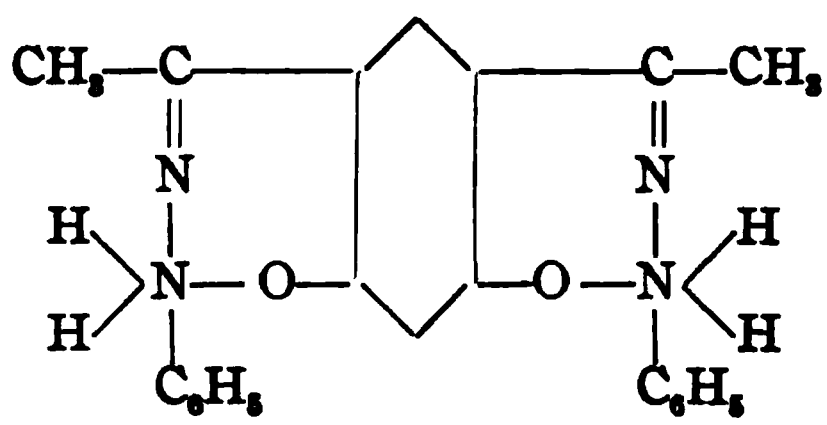
[2] Position of Br not proved.

$$-\overset{\overset{\displaystyle CH_3}{|}}{C} = N - NHC_6H_5;$$

(2) other substituting groups are present, as OCH_3 or $OOCC_6H_5$, etc. If the basic group substituting the ketone oxygen is small, as in the bis-azine or resodiacetophenone, the compound is soluble. Although Anselmino found that the phenylhydrazone of homosalicylaldehyde was insoluble in alkalies, K. Auwers and R. Bondy[1] have found that the phenylhydrazone of 5-nitro-2-hydroxy-1-methyl-3-benzaldehyde is soluble, while the same derivative of 5-nitro-4-hydroxy-1-methyl-3-benzaldehyde dissolves with difficulty, although we prepared phenylhydrazones from nitrated paeonol and from methylated nitroresoacetophenone. We have omitted them from the experimental part of this paper, as they have not as yet been sufficiently studied. The introduction of a less negative group, as bromine, into the ring, does not affect the solubility, for we found the bisphenylhydrazone of bromresodiacetophenone to be insoluble in alkalies.

It is, in our opinion, impossible to give at the present time an adequate explanation of the alkali-insolubility of these compounds.

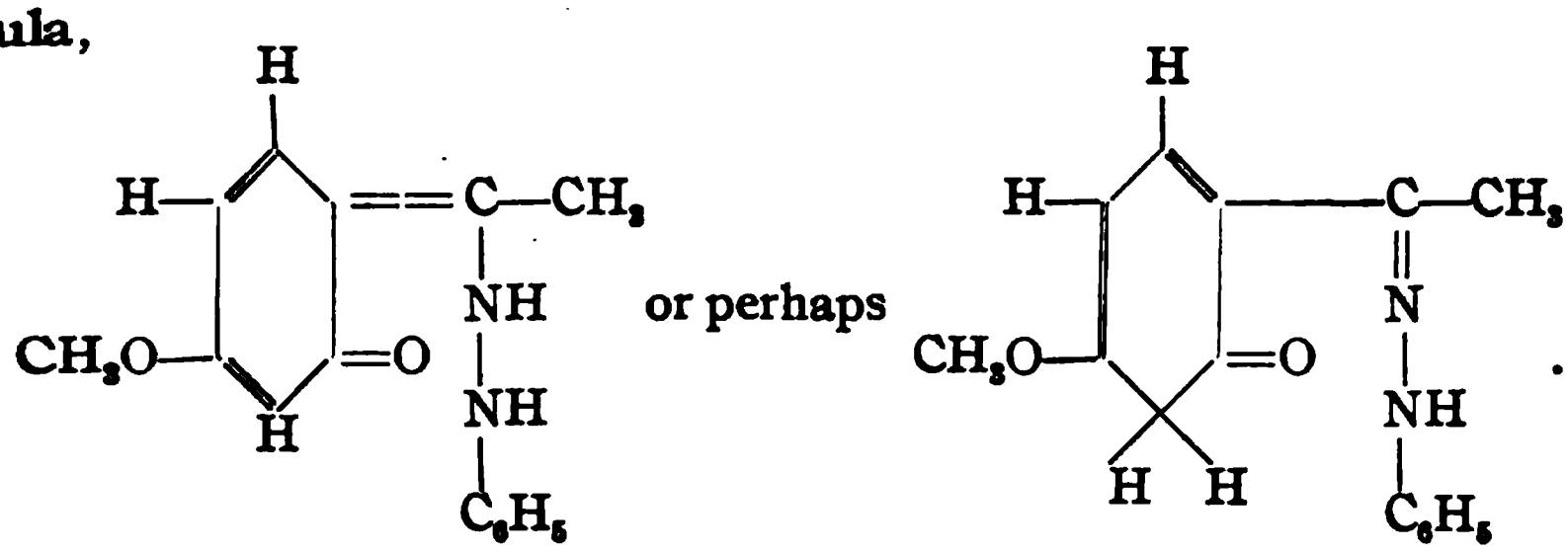
Anselmino, in discussing the insoluble aldehyde derivatives, shows that no secondary condensation between the imide and hydroxyl group has taken place and calls attention to the fact that E. Fischer[2] has shown to be erroneous the statement of Causse[3] that such a condensation occurs between salicylaldehyde and phenylhydrazine in the presence of acetic anhydride. Not only do our analytical results show that in the phenylhydrazones recorded by us no such secondary condensation has occurred, but it is evident that no condensation of the kind could take place in the alkali-insoluble aniline and benzidine derivatives. This hypothesis is thus made untenable. A second hypothesis is that an inner salt has been formed, which, with the bisphenylhydrazone of resodiacetophenone, would be formulated as follows:



The comparatively weak acid nature of resodiacetophenone and the ortho hydroxy ketones studied makes such a hypothesis seem extremely

[1] *Ber.*, 37, 3915.
[2] *Ibid.*, 30, 1240.
[3] *Compt. rend.*, 124, 505.

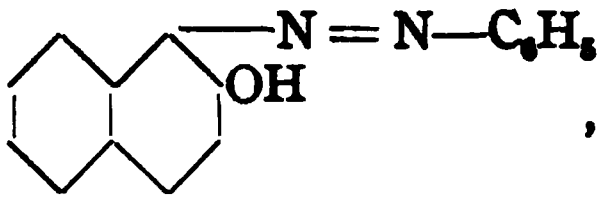
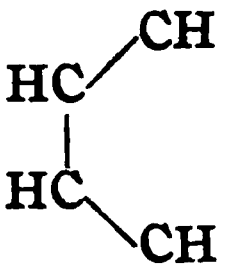
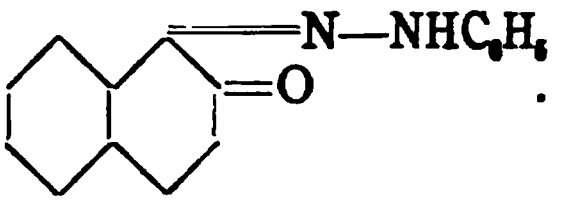
unlikely, and further, it would offer no explanation for the difference in solubility in alkalies between the phenylhydrazone of *o*-hyroxyacetophenone and the phenylhydrazone of paeonol, or especially between the phenylhydrazone of salicylaldehyde and that of homosalicylaldehyde. In order to give some test to this theory, we have introduced a bromine atom into each of the phenylhydrazone groups in the bisphenylhydrazone of resodiacetophenone, thereby increasing the negativity of these groups and consequently decreasing the tendency toward salt formation, but without effect upon the solubility. It might be suggested that the insolubility is due simply to the fact that the acid nature of the phenol has been highly depressed by the introduction of basic groups, such as the phenylhydrazone or benzidine groups. If this were the true explanation, we should expect the phenylhydrazones of paeonol, or of the acetates or benzoates of resacetophenone and resodiacetophenone to be more soluble in alkalies than the phenylhydrazones of *o*-hydroxyacetophenone or of salicylaldehyde instead of less soluble. The alkali-insolubility of the compounds, then, cannot be explained by the hydrolytic action of water, especially when one considers that the bisphenylhydrazone of resodiacetophenone is not dissolved by a solution of sodium hydroxide of as great strength as 1:1. It was suggested in a former paper[1] that these compounds may have a quinoid structure and that the insolubility is due to this; thus for paeonol phenylhydrazone we have the formula,



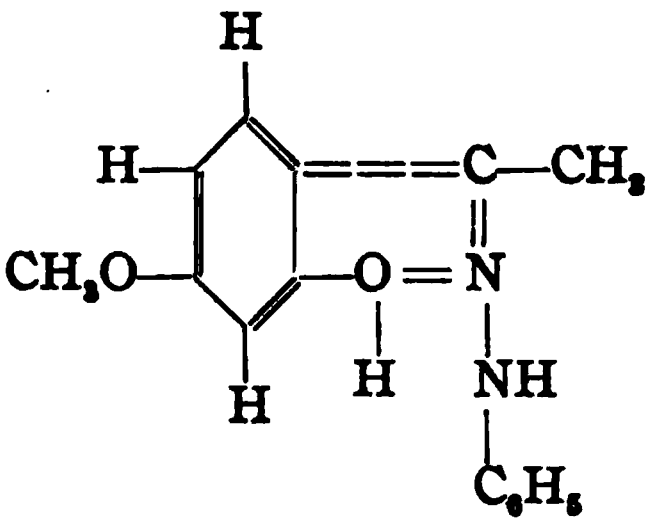
We have been unable, however, to get any indication of such quinoid oxygen by the action of hydroxylamine, although it should be said that even if such a quinoid oxygen were present, it would be unlikely to react with hydroxylamine, and Anselmino[2] has shown that in the phenylhydrazones of the homosalicylaldehydes which are insoluble in aqueous alkalies, the phenylhydrazone group reacts with pyruvic acid to give its hydrazone, and that the phenol oxygen can be benzoylated by benzoyl chloride in pyridine solution. We are not, however, yet ready to entirely abandon the quinoid formulas as a possibility. The alkali-insoluble phenols that we have studied bear a certain analogy to 2-naphthol-1-

[1] THIS JOURNAL, 29, 77.

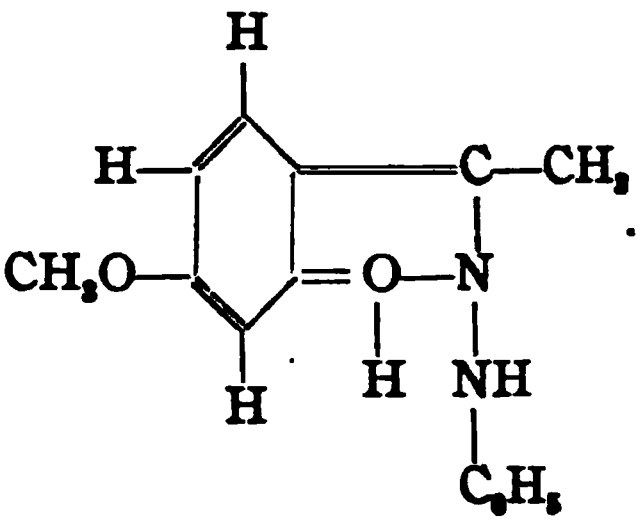
[2] *Ber.*, 35, 4101.

azobenzene,  , which is insoluble in aqueous alkalies, and in which the four carbon chain  has the same influence on the solubility as the carbon-containing groups in our compounds. A. Goldschmidt and R. Brubacher,[1] by a study of the reduction products of its acetyl and benzoyl derivatives, have shown that in all probability this substance actually has this quinoid structure  .

Fosse and Robyn[2] attribute the alkali-insolubility of the rather different compounds studied by them to the presence of a quadrivalent oxygen atom. If we assume that in our compounds, the oxygen of the hydroxyl is quadrivalent, the formula for the phenyl hydrazone of paeonol, for instance, might be written thus:



or



Since, however, quadrivalent oxygen ordinarily shows basic properties, such constitutions as these seem unlikely.

A very striking fact regarding the alkali-insoluble phenols is that although they are insoluble in aqueous alkalies they all dissolve with great ease in *alcoholic* alkalies and may be precipitated by mineral acids from these solutions unchanged.

In general, one may say regarding the alkali-insolubility of the phenols, that it is due to the combined influence of a large group as

$$-\overset{\overset{\displaystyle H}{|}}{C}=N-\overset{\overset{\displaystyle H}{|}}{N}C_6H_5,\ -\underset{\underset{\displaystyle CH_3}{|}}{C}=N-\overset{\overset{\displaystyle H}{|}}{N}C_6H_5,\ \text{etc.},$$

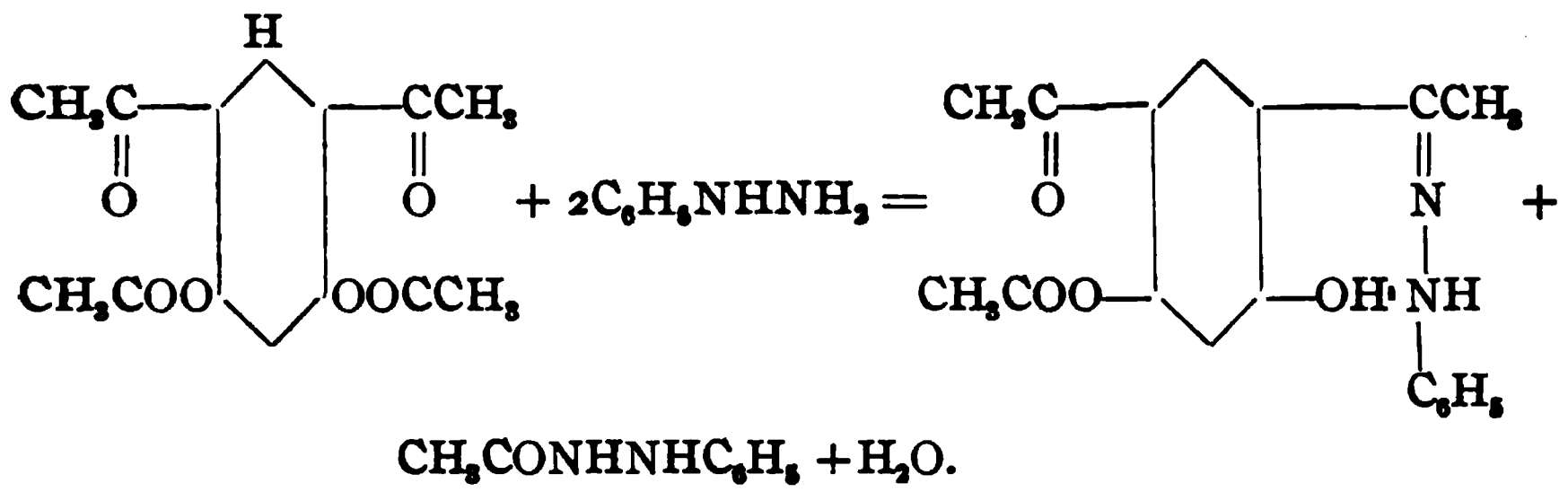
in the ortho position to the hydroxyl and a carbon-containing group else-

[1] *Ber.*, **24**, 2306.

[2] *Loc. cit.*

where in the ring. Whether the insolubility is due to an actual change in structure cannot at present be stated.

In the course of this work we have noticed some interesting cases of so-called steric hindrance, particularly in connection with the action of phenylhydrazine on resodiacetophenone diacetate and dibenzoate. When two molecules of phenylhydrazine were allowed to act on one molecule of resodiacetophenone diacetate in a hot alcoholic solution, containing acetic acid, the product obtained was the monophenylhydrazone of resodiacetophenone monoacetate, instead of the bisphenylhydrazone of the diacetate. The reaction proceeded, then, according to the following equation:

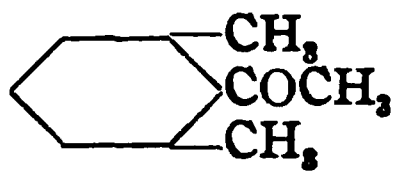


$$CH_3CONHNHC_6H_5 + H_2O.$$

The acetylphenylhydrazine formed in the reaction was isolated from the mother liquor. If a large excess of phenylhydrazine, not less than four molecules, for example, was allowed to act on the diacetate under the same conditions, both acetyl groups were eliminated with the formation of resodiacetophenone bisphenylhydrazone. The action of phenylhydrazine on the dibenzoate of resodiacetophenone is exactly analogous to its action on the diacetate. In an earlier paper[1] we stated that phenylhydrazine, acting upon resacetophenone dibenzoate gave the phenylhydrazone of the dibenzoate, melting at 183°. We have found, however, that this is erroneous, and that here also the benzoyl group adjacent to the keto side chain is eliminated, giving the phenylhydrazone of resacetophenonemonobenzoate. We experienced great difficulty in the determination of carbon in this compound, the results being generally about two per cent. high, until the method described in the experimental part of the paper was adopted. A more convenient way to prepare the same compound is to introduce the benzoyl group into resacetophenone phenylhydrazone, by means of the Schotten-Baumann reaction. Even though more than two molecules of benzoyl chloride were used, only one benzoyl group was introduced, since the hydroxyl group adjacent to the large side chain was protected from the action of the reagent.

Somewhat similar interference phenomena were noticed in attempting to prepare the bisphenylhydrazone of resodiacetophenonedimethyl ether.

[1] This Journal, 29, 80.

When the proper amount of phenylhydrazine was allowed to stand with the dimethyl ether in hot or cold alcohol or alcohol and acetic acid, only the unchanged resodiacetophenonedimethyl ether was obtained after crystallization from dilute alcohol. Other examples of hindrance of this kind are not wanting; for instance, Baum[1] and v. Meyer[2] have found that ketonic compounds of the type  do not react with the phenylhydrazine, and Klinger and W. Kolvenbach[3] were unable to obtain a phenylhydrazone from acetohydroquinone, although its dibenzoate gave a phenylhydrazone. On the other hand, we obtained the bisphenylhydrazone from the monomethyl ether of resodiacetophenone and from dibenzohydroquinone and dibenzoresorcinol.[4] In attempting to methylate the hydroxyl groups in the bisphenylhydrazone of resodiacetophenone, by acting upon its solution in alcoholic potash with methyl iodide, merely the unchanged hydrazone or its saponification products were obtained. Anselmino also found it impossible to methylate the phenylhydrazones of the homosalicylaldehydes.

In the latter part of this paper we describe the action of metanitrobenzoyl chloride upon hydroquinone diacetate and resorcinol diacetate in the presence of condensing agents such as anhydrous aluminium chloride, but we were entirely unsuccessful in our attempt to introduce the nitrobenzoyl group into the ring itself, in every case either one or both of the acetyl groups being replaced by the nitrobenzoyl group. Thus, from resorcinol diacetate, $C_6H_4(OOCCH_3)_2$, resorcinol *m*-nitrodibenzoate, $C_6H_4(OOCC_6H_4NO_2)_2$, was obtained. This replacement may be due, in part at least, to the greater volatility of acetyl chloride as compared with nitrobenzoyl chloride, and might be compared to the action of sulphuric acid on sodium chloride. Other analogous organic metathetical reactions have been observed, as for instance, the displacement of the acetyl group in acetaniline by the action of benzoyl chloride,[5] the formation of ethyl acetate by heating amyl acetate with ethyl alcohol at 240°, and of amyl benzoate by heating ethylbenzoate with amyl alcohol,[6] similar replacements by means of alcoholates,[7] the displacement of the methyl group[8] by the action of acetyl chloride and aluminium chloride

[1] *Ber.*, 28, 3207.

[2] *Ibid.*, 29, 835.

[3] *Ibid.*, 31, 1216.

[4] THIS JOURNAL, 29, 81.

[5] Paal and Otten, *Ber.*, 23, 2587; and Ame Pictet, *Ibid.*, 23, 3011.

[6] Friedel and Crafts, *Ann.*, 133, 208.

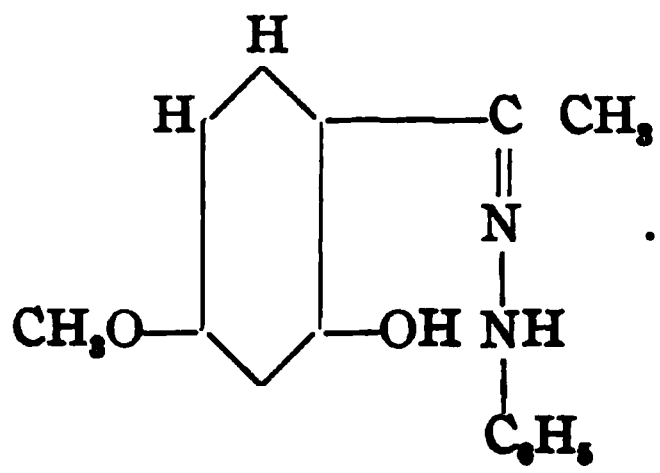
[7] J. Purdie, *Ber.*, 20, 1554. Gattermann and Ritschke, *Ibid.*, 23, 1738. Jackson and Torrey, *Am. Chem. J.*, 20, 404.

[8] Claus and Huth, *J. pr. Ch.* [2], 53, 59.

and the replacement of the isobutyryl[1] by the acetyl group, and especially the formation of phenyl benzoate from phenyl acetate by the action of benzoyl chloride in the presence of zinc chloride.[2]

Experimental Part.

4-Monomethyl Ether of Resacetophenone Phenylhydrazone.—On shaking a molecule of resacetophenone phenylhydrazone[3] with slightly more than one molecule of dimethylsulphate in alkaline solution for eight hours, a compound was obtained which melted at 108° and was insoluble in ammonia and aqueous alkalies. Analysis showed that it was the monomethyl ether of resacetophenone phenylhydrazone; and since it is identical with the phenylhydrazone of paeonol, the methoxy group must be in the para position to the side chain:



. It is soluble in alcohol, benzene, ether, chloroform, acetic acid, and alcoholic sodium or potassium hydroxide. It was purified by crystallization from dilute alcohol.

Calculated for $C_{15}H_{16}O_2N_2$: C, 70.31; H, 6.25.
Found: C, 70.03; H, 6.34.

Paeonol,[4] an aromatic ether, occurring in the root-bark of *Paeonia Moutan*, has been used for medicinal purposes in Japan and China since the earliest times. W. Nagai[5] showed that it was the 4-monomethyl ether of resacetophenone and Tahara[6] synthesized it from resacetophenone and found that the hydroxyl group ortho to the aceto group was methylated with some difficulty. In order to compare the product of the methylation of the phenylhydrazone of resacetophenone with the phenylhydrazine obtained from paeonol itself, the latter compound was prepared by allowing one molecule of resacetophenone, dissolved in dilute alkali, to stand for several days with one molecule of dimethyl sulphate. By using a shaking machine, the results were much more rapid and satisfactory. After acidifying, the paeonol was extracted with benzene, in which it is much more soluble than is resacetophenone. After evaporation of the solvent, the paeonol was purified by distillation *in vacuo*;

[1] Brauchbar and Kohn, *Monatsh.*, 19, 27.
[2] Döbner, *Ann.*, 210, 255.
[3] *Bull. Soc. Chem.* [3], 6, 154.
[4] *Ber.*, 25, 1292.
[5] *Ibid.*, 24, 2847.
[6] *Ibid.*, 24, 2460.

under 30 mm. the paeonol came over at about 210° and under 5 mm. at 180°. The crystals which formed on cooling melted at 50–51°. The phenylhydrazone of paeonol has already been described by F. Tiemann,[1] but was prepared by us for the sake of comparison and, as has been said, was identical with the monomethylether of resacetophenone phenylhydrazone described above.

The Phenylhydrazone of Resacetophenonemonobenzoate,

(4) $C_6H_5COOC_6H_3\left\langle\begin{matrix}OH\ (2)\\ CCH_3N_2HC_6H_5\ (1)\end{matrix}\right.$.—By allowing the alkaline solution of the phenylhydrazone of resacetophenone to stand for several days at room temperature with more than two molecules of benzoyl chloride, a compound was obtained which was insoluble in cold aqueous alkalies, although solution with accompanying saponification takes place slowly. The insoluble precipitate was collected upon a filter, dried with suction and upon a clay plate. The benzoate was crystallized from hot alcohol, there being a considerable difference between the solvent powers of the hot and the cold solvent. M. p. 181–2°. It is also soluble in benzene and glacial acetic acid; in aqueous sodium hydroxide it is insoluble, but dissolves slowly on boiling. This compound was described in an earlier paper[2] as the phenylhydrazone of resacetophenone dibenzoate, since the analytical results pointed to this formula, but our subsequent work upon it has shown it to be the monobenzoate. Great difficulty was experienced in the combustion of this substance, the results for carbon usually being too high for the monobenzoate. Satisfactory results were finally obtained by proceeding as follows: The substance was mixed with fine copper oxide, and two reduced copper spirals were placed in the front part of the combustion tube. Before beginning the burning, a tube containing a reduced copper spiral was attached to the forward end of the combustion tube and dry air, free from carbon dioxide, was passed over this hot spiral, until the combustion tube proper was filled with an atmosphere rich in nitrogen and containing little oxygen. The special tube containing the copper spiral was then replaced by the absorption apparatus and the combustion was begun. The substance was heated very gradually and, as the burning progressed, oxygen was introduced into the tube. In two determinations a little oxygen was introduced into the rear end of the tube early in the combustion.

Calculated for $C_{21}H_{18}O_3N_2$: C, 72.83; H, 5.20; N, 8.09.
Found: C, 74.77, 73.96, 72.53, 72.92, 72.38, 72.75; H, 4.91, 6.08, 3.85, 6.15, 4.43, 5.41; N, 8.56, 7.84, 8.25, 7.99.

This same compound was also obtained from the resacetophenone diben-

[1] *Ber.*, 24, 2854.
[2] THIS JOURNAL, 29, 80.

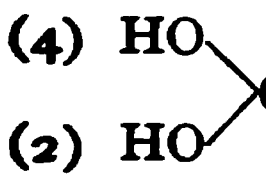
zoate[1] by the action of phenylhydrazine in hot alcoholic solution, which shows that the benzoyl group has replaced the hydrogen of one of the hydroxyl groups and not that of the imido group. The removal of one benzoyl group is in accord with our observations on the action of phenylhydrazine on resodiacetophenone diacetate and dibenzoate, described below, and it is reasonably certain that the benzoyl group removed is that nearest the ketone side chain.

The Phenylhydrazone of Resacetophenonemonoacetate.—One molecule of resacetophenonemonoacetate,[2] treated with slightly more than one molecule of phenylhydrazine in hot dilute alcohol containing some acetic acid, gave a compound melting at 127–8°. It is slowly dissolved in aqueous alkalies with the probable saponification of the acetyl radical. It is soluble in alcohol and less so in ether and chloroform; insoluble in benzene. It was crystallized for analysis from alcohol.

Calculated for $C_{16}H_{16}O_2N_2$: N, 9.86.
Found: N, 9.38.

The action of phenylhydrazine on resacetophenonediacetate[3] as well as the action of hot acetic anhydride on the phenylhydrazone of resacetophenone, gave a thick, viscous product, which could not be obtained in a crystalline form.

Mononitroresacetophenone Phenylhydrazone,

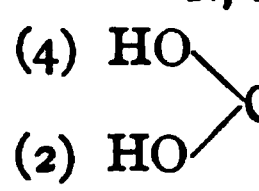


$(4)\ HO \diagdown C_6H_2NO_2C.CH_3N_2HC_6H_5(1)$
$(2)\ HO \diagup$

.—The phenylhydrazone of mononitroresacetophenone was obtained by dissolving the mononitroresacetophenone[4] in hot alcohol and adding slightly more than one molecule of phenylhydrazine. On cooling, beautiful dark red crystals separated out, which, after crystallization from alcohol and acetic acid, melted at 232–4° with decomposition. It is somewhat soluble in hot benzene or toluene with a brownish color, and in hot alcohol or chloroform with a reddish color. It dissolves in glacial acetic acid with a reddish color and may be precipitated by water. As would be expected, it is soluble in alkalies; the precipitate obtained by neutralizing this solution with hydrochloric acid at first appears yellowish brown, but with an excess of acid rapidly becomes red in color.

Calculated for $C_{14}H_{13}O_4N_3$: N, 14.63.
Found: N, 14.11.

Resacetophenone Semicarbazone,



$(4)\ HO \diagdown C_6H_3C:CH_3N_2HCONH_2(1)$
$(2)\ HO \diagup$

.—

[1] Torrey and Kipper: THIS JOURNAL, 29, 80.
[2] *J. pr. Chem.* [2], 23, 149; *Am. Chem., J.*, 7, 276.
[3] *Ber.*, 30, 297.
[4] *J. pr. Chem.* [2], 23, 151.

An aqueous solution containing rather more than one molecule of semicarbazide hydrochloride, together with an equivalent quantity of sodium acetate, was added to one molecule of resacetophenone dissolved in alcohol. The mixture was shaken for some time. After filtration the reaction product was dried on a porous plate and crystallized from benzene. Yellow needles, melting with gradual decomposition at 214–220°, were obtained. The semicarbazone is soluble in alcohol, ether, and hot benzene, and is soluble in chloroform. It is soluble in ammonia and aqueous alkalies.

Calculated for $C_9H_{11}O_3N_3$: N, 20.09.
Found: N, 19.34.

The Preparation of Resodiacetophenone.—The method used for making resodiacetophenone was essentially that employed by Crespieux.[1] One and one-half molecules of anhydrous zinc chloride were dissolved in one and one-half molecules of glacial acetic acid, and to this hot mixture one molecule of resacetophenone was added, after which the whole was heated to 140° in an oil-bath. From a dropping funnel one molecule of phosphorus oxychloride was run slowly into the mixture, while the heating at 140° was continued for one-half hour. The hot, viscous product was then poured into water; the resodiacetophenone separating out was filtered from the soluble zinc salts and crystallized from alcohol. It was found that a shorter heating (3–5 minutes) at 140–150° after the addition of the phosphorus oxychloride was advantageous. While adding the phosphorus oxychloride care must be taken not to allow the temperature to rise above 150°, as carbonization is likely to take place. A mixture of alcohol and benzene was found more advantageous than pure alcohol for the crystallization of the resodiacetophenone, as it was found easier to separate it from a reddish substance, probably resacetein, formed at the same time. When the latter had been formed in considerable amounts, benzene was used with advantage as a crystallizing medium, as the red-colored impurity is practically insoluble even in hot benzene. It is desirable, however, to carry out the first crystallization in alcohol. By fusing resorcinol diacetate with anhydrous zinc chloride, J. F. Eijkmann[2] obtained a diacetodihydroxyphenone, which proves to be identical with the resodiacetophenone made according to the method given above. Eijkmann[3] showed that the same methoxyethoxydiacetophenone was obtained in each case, whether the methoxyhydroxydiacetophenone was ethylated or the ethoxyhydroxydiacetophenone was methylated; further, by oxidation of dimethoxydiacetophenone with potassium permanganate, 4,6-dimethoxyisophthalic acid, $C_6H_2(COOH)_2^{1,3}(OCH_3)_2^{4,6}$,

[1] *Bull. Soc. Chim.* [3], 6, 152.
[2] *Chem. Centr.*, 1904, I, 1597
[3] *Ibid.*, 1905, I, 814.

was obtained, showing conclusively the constitution of the dihydroxydiacetophenone to be $C_6H_2(COCH_3)_2^{1,5}(OH)_2^{2,4}$.

The identity of resodiacetophenone, made as given above, with this dihydroxydiacetophenone, was shown by making the mono- and dimethyl ethers by the action of methyl iodide on an alcoholic solution of the potassium salt of resodiacetophenone. These melting-points were found to be 120° and 170°, respectively, the same as given by Eijkmann. Further, the phenylhydrazones of both compounds were found to be identical in properties.

Salts of Resodiacetophenone.—Resodiacetophenone, when dissolved in that quantity of sodium hydroxide which gave two molecules of the latter to one of the former, and evaporated to dryness on the steam-bath, gave the white sodium salt. If lead acetate was added to some of the above solution, a pinkish precipitate of the lead salt was obtained. The addition of silver nitrate gave a white precipitate which blackened rapidly in the air.

Resodiacetophenone Bisphenylhydrazone, 2,4-Dihydroxy-1,5-Diacetophenone Bisphenylhydrazone, $C_6H_2(OH)_2(C.CH_3N_2HC_6H_5)_2$.—This substance was discovered by Crespieux[1] and has been described by us also in a recent paper.[2] It is best prepared by allowing considerably more than two molecules of phenylhydrazine to stand for several hours with an alcoholic solution of resodiacetophenone. The substance crystallized from aniline, diethyloxalate, acetone and alcohol, all gave the same melting-point, namely 291°. This is 60° higher than that given by Crespieux. Work which is now being carried on in the laboratory by Mr. R. D. Bell and one of us has shown that varying quantities of resodiacetophenone monophenylhydrazone are formed together with the bisphenylhydrazone, even when a large excess of phenylhydrazine is used and the mixture is allowed to stand for some time. Such mixtures melt at about 230°, but after treatment with a sodium hydroxide solution, which dissolves out the monophenylhydrazone without having the slightest effect upon the bisphenylhydrazone, the melting-point is immediately raised. That it is the resodiacetophenone monophenylhydrazone which is dissolved out by the alkali was shown by precipitating the filtrate with acid and analyzing the product after crystallization from diethyl oxalate. The insolubility of resodiacetophenone bisphenylhydrazone in even the most concentrated aqueous alkalies is very marked. It is, however, easily soluble in alcoholic sodium or potassium hydroxide, giving a yellow solution, from which the original compound, together with small quantities of a decomposition product, namely, the monophenylhydrazone, may be precipitated by mineral acids. If acetic acid was

[1] *Bull. Soc. Chim.* [3], 6, 152.

[2] THIS JOURNAL, 29, 80.

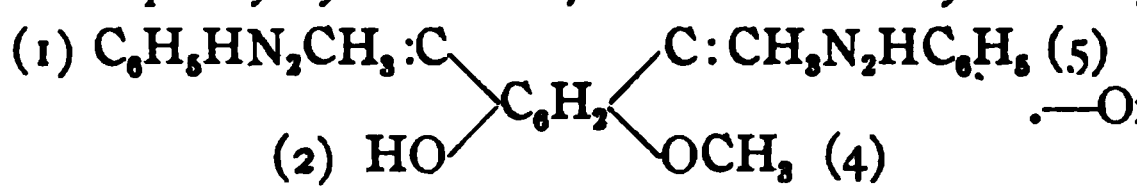
used, instead of hydrochloric, the precipitate, as it stood in the liquid, appeared almost white. The modification obtained by crystallization from aniline had a rather deep orange color.

The Monophenylhydrazone of Resodiacetophenone, 2,4-Dihydroxy-1,5-Diacetophenone Monophenylhydrazone, $C_6H_2(OH)_2COCH_3.CCH_3NNHC_6H_5$. —This compound was obtained exactly as the bisphenylhydrazone, except that only a little more than one molecule of phenylhydrazine to one of resodiacetophenone was employed. The light yellow crystals which separated out were collected on a filter, washed, and then dissolved in 10 per cent. sodium hydroxide, to free them from the small amount of bisphenylhydrazone formed, which is insoluble in aqueous alkalies. After filtration the hydrazone was precipitated with hydrochloric acid. The precipitate was washed with hot water and finally with alcohol, dried on a porous plate and crystallized from brombenzene, in which the monohydrazone is very soluble when hot and but slightly so in the cold. Light yellow needles, melting with decomposition at 233°, were obtained. By crystallization from hot acetone, in which the solubility is also high, yellow, tetragonal plates were formed, likewise melting at 233°.

Calculated for $C_{16}H_{16}O_3N_2$: N, 9.86.
Found: N, 9.58.

This monohydrazone is soluble in ammonia and aqueous alkalies with a yellow color. It is soluble in acetic acid, hot and cold, and precipitated from this solution by water. It is slightly soluble in hot or cold alcohol, benzene, or chloroform, and readily soluble in hot acetone and ethyl acetate.

Bisphenylhydrazone of the Monomethylether of Resodiacetophenone,

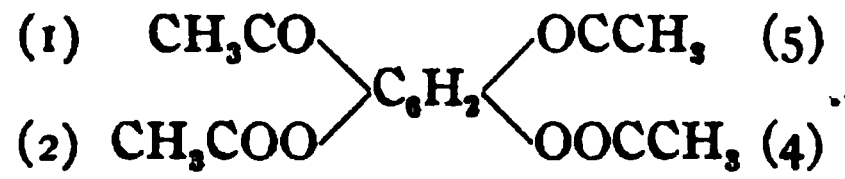


.—One molecule of the monomethyl ether of resodiacetophenone, dissolved in hot alcohol, was heated on a steam-bath for a short time with slightly more than two molecules of phenylhydrazine. A light yellow precipitate began to appear very soon, and after cooling and allowing to stand for a few hours, an almost quantitative yield of the hydrazone was obtained. It was crystallized from benzene, in which it is quite soluble when hot. Long, transparent needles were obtained, melting at 245–6°, with decomposition, which were insoluble in aqueous alkalies.

Calculated for $C_{23}H_{24}O_2N_4$: N, 14.43.
Found: N, 14.18.

When the dimethyl ether of resodiacetophenone was treated with phenylhydrazine in hot or cold alcohol or in alcohol and acetic acid, no action took place, as the product, after crystallization from dilute alcohol, proved to be merely unchanged resodiacetophenone dimethyl ether.

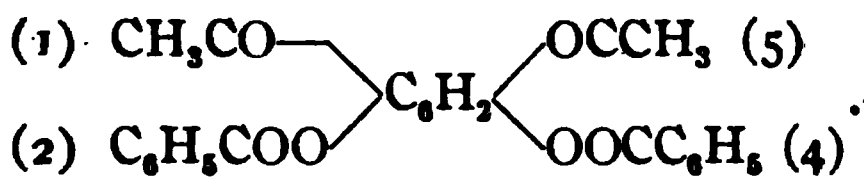
Resodiacetophenone Diacetate (*1,5-Diacetophenone Diacetate-2,4*),



.—Five grams of resodiacetophenone were dissolved in about 30 grams of acetic anhydride and boiled for two hours under a reflux condenser. The solution was allowed to cool and filtered from the precipitate which separated. After drying and crystallization from alcohol, colorless needles, melting at 120°, were obtained, while from benzene the compound crystallized in transparent hexagonal plates. It is readily soluble in chloroform and in hot alcohol or benzene, and is far more soluble in cold benzene than is resodiacetophenone.

Calculated for $C_{14}H_{14}O_6$: C, 60.43; H, 5.04.
Found: C, 60.15; H, 5.56.

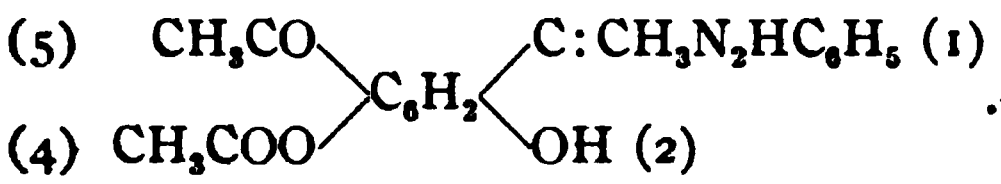
Resodiacetophenone Dibenzoate (*1,5-Diacetophenone Dibenzoate*),



.—It was found possible to prepare the dibenzoate by heating resodiacetophenone with benzoyl chloride at 170–180°, but much better results were obtained by the following method, which gave an almost quantitative yield: Five grams of resodiacetophenone were dissolved in thirty grams of warm pyridine, the solution was then cooled in ice-water, at which temperature some resodiacetophenone separated, and a little more than two molecules of benzoyl chloride were added in small portions with constant shaking. The mixture was then allowed to come to room temperature and finally heated just enough to make the solution complete. After allowing to cool again, first water and then a solution of sodium carbonate were added and the dibenzoate was washed with ammonia. Drying and crystallization from alcohol gave a constant melting-point of 118–9°. It is soluble in benzene, alcohol and chloroform, but more so in the hot than in the cold solvent; it is also soluble in hot and cold glacial acetic acid and very soluble in hot toluene. It is readily saponified by boiling with a ten per cent. sodium hydroxide solution.

Calculated for $C_{24}H_{18}O_6$: C, 71.64; H, 4.48.
Found: C, 71.48; H, 5.25.

Monophenylhydrazone of Resodiacetophenone Monoacetate,

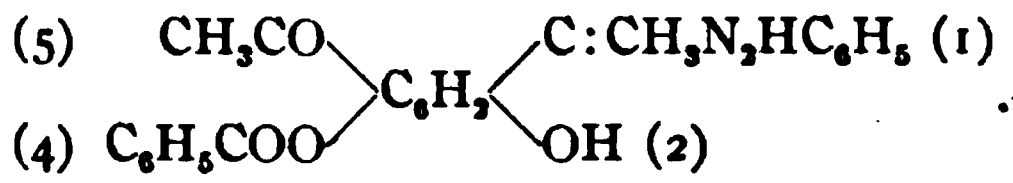


.—Two molecules of phenylhydrazine were allowed to act on one of resodiacetophenone diacetate dissolved in a mixture of hot acetic acid and alcohol. On cooling, a heavy white precipitate fell, which after filtration, drying on a porous plate, and crystallization from benzene, was obtained in the form of transparent plates,

melting, when pure, at 191–2°; from alcohol it crystallized in white needles, giving the same melting-point. In the mother liquor, from the preparation of this compound, acetylphenylhydrazine,[1] $C_6H_5NHNHCOCH_3$, was isolated, proving that one at least of the acetyl groups must have split out. The interference of these groups is shown in an even more marked degree by the action of four molecules of phenylhydrazine, when both acetyl groups are removed and the bisphenylhydrazine of resodiacetophenone is formed. The monophenylhydrazone of resodiacetophenone monoacetate is rather soluble in hot alcohol and benzene, but only slightly so in these solvents when cold; very soluble in hot toluene; soluble in glacial acetic acid, and precipitated with water. It dissolves slowly in cold sodium hydroxide, rapidly on boiling, with decomposition. By acidification of the solution from the action of either hot or cold hydroxide, resodiacetophenone monophenylhydrazone, m. p. 233°, was obtained. Since the solution has the odor of phenylhydrazine, it is evident that a small amount of this group is also split out.

Calculated for $C_{18}H_{18}O_4N_2$: N, 9.59.
Found: N, 8.70, 9.15.

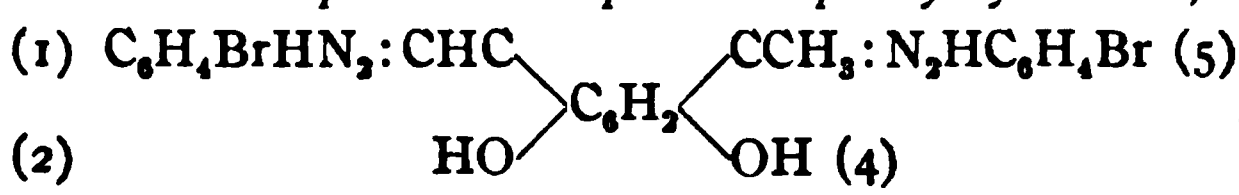
Monophenylhydrazone of Resodiacetophenone Monobenzoate,



.—The action of phenylhydrazine on the dibenzoate of resodiacetophenone is exactly analogous to its action on the diacetate described above. Two molecules of phenylhydrazine react with one molecule of the dibenzoate in hot alcoholic solution, and on cooling a white compound separates, which after crystallization from alcohol finally gives colorless, transparent prisms, with constant melting-point of 214-5°. The compound is soluble in hot alcohol, benzene and chloroform, but less so in the cold. It may be precipitated from its acetic acid solution by water. It is insoluble in ammonia and in ten per cent. sodium hydroxide, the solvent action is very slow in the cold, but rather rapid on boiling, when doubtless saponification takes place. It will be seen that in the formation of this hydrazone, one benzoyl group has been removed by the action of the phenylhydrazine.

Calculated for $C_{23}H_{20}O_4N_2$: N, 7.22.
Found: N, 7.23, 7.49.

Resodiacetophenone Bisparabromphenylhydrazone,



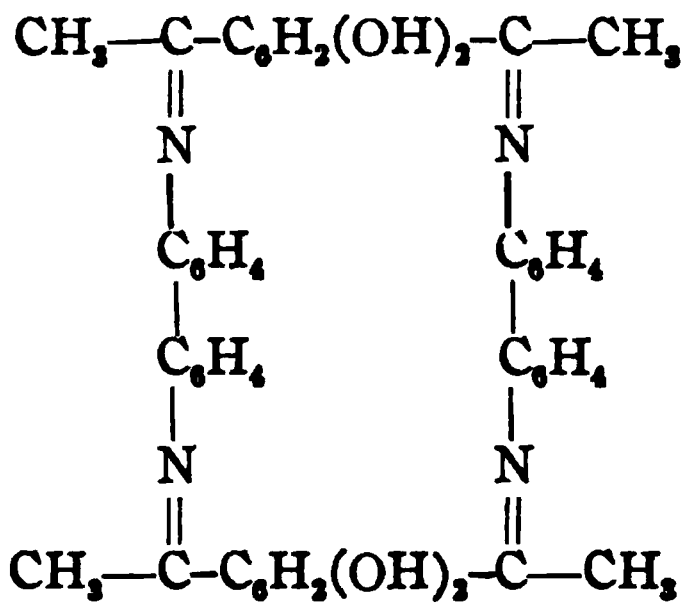
.—An alcoholic solution of two molecules of *p*-bromphenylhydrazine and one of resodiacetophenone was boiled on the steam-bath under a reflux condenser for one

[1] *Ann.*, 190, 129.

hour. The light yellow needles thus obtained were purified by crystallization from acetone, in which the compound is fairly soluble in the hot and less so in the cold. It melted at 270–1° with decomposition. It is readily soluble in hot nitrobenzene, aniline and monobrombenzene, but slightly so in these solvents when cold; insoluble in alcohol, benzene, chloroform, toluene, ligroin, and amyl alcohol; slightly soluble in hot acetic acid and ethyl acetate. It is insoluble in ammonia and aqueous alkalies, but soluble in alcoholic sodium hydroxide; boiling with very strong potassium hydroxide (1 : 1) causes decomposition.

Calculated for $C_{22}H_{20}O_2N_4Br_2$: Br, 30.07.
Found: Br, 29.88.

Addition and Substitution Products Obtained from the Interaction of Resodiacetophenone and Benzidine.—One molecule of resodiacetophenone was dissolved in hot alcohol and to this a hot alcoholic solution of two molecules of benzidine was added and the mixture was heated for about one hour on the steam-bath under a reflux condenser. A precipitate of yellow crystals was obtained which was filtered while the liquid was still hot and was washed with hot alcohol. This product, which melted above 300° was insoluble in the ordinary solvents, but soluble in hot aniline, monobrombenzene or nitrobenzene, the last two solvents causing a slight browning; it is not decomposed by ammonium hydroxide, but hot acetic acid causes gradual decomposition and boiling with a ten per cent. sodium hydroxide solution decomposes it slowly and concentrated hydrochloric acid causes a fairly rapid hydrolysis. From aniline, light yellow needles, melting above 300°, were obtained, which proved, on analysis, to be a condensation product of benzidine and resodiacetophenone in the proportion of one molecule of each. Because of the marked insolubility in all the ordinary solvents, no attempt was made to determine the molecular weight. Since in condensation of benzidine with aldehydes and ketones both amine groups commonly enter into the reaction and from analogy to the azine derivative described below, it appears most likely that two molecules of benzidine have reacted with two molecules of resodiacetophenone, giving a compound of the following formula:

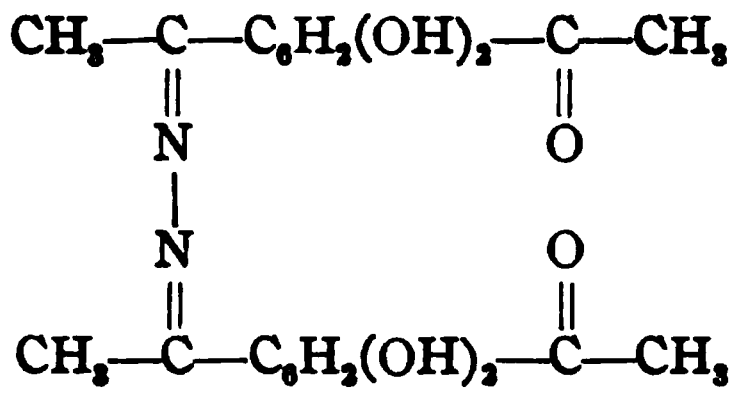


Calculated for $C_{34}H_{36}O_4N_4$: C, 77.19; H, 5.26; N, 8.19.
Found: C, 77.31; H, 5.82; N, 8.22.

From the alcoholic filtrate from the preparation of the above benzidine derivative, yellow needles separated on cooling, which were washed with cold alcohol. These melted slowly between 182° and 185° with decomposition; a second and a third rapid crystallization from alcohol gave the same melting-point, as well as crystallization from benzene. Since the two reacting substances, benzidine and resodiacetophenone, are both colorless, and the product obtained consisted of beautiful, well-shaped, yellow crystals, it is not possible that it is simply a mixture of these two substances. It is readily decomposed on standing with aqueous ammonia or acetic acid, with the former benzidine being precipitated and resodiacetophenone passing into solution, while with the latter resodiacetophenone is precipitated and benzidine dissolved. On boiling the alcoholic or benzidine solution of the low-melting derivative for several hours under a reflux condenser, a yellow precipitate is formed, having the properties of the high-melting condensation product. The properties and the analysis of the soluble low-melting compound indicate that it is an addition product of one molecule of benzidine with four molecules of resodiacetophenone.

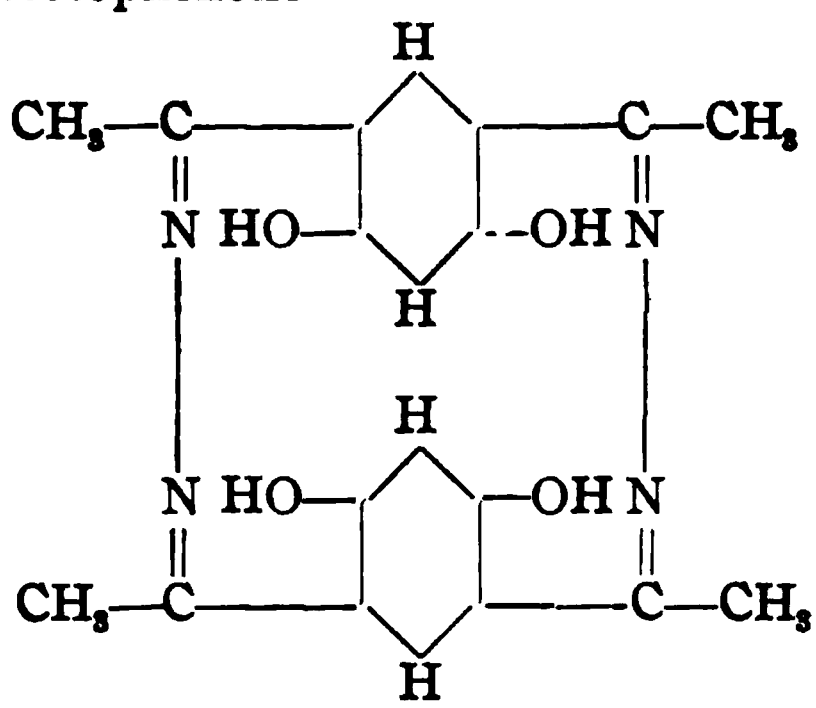
Calculated for $C_{12}H_{12}N_2.4C_{10}H_{10}O_4$: N, 2.92.
Found: N, 2.36, 2.64.

The Mono- and bis-Azine Derivatives of Resodiacetophenone and an Aniline Condensation Product Obtained from the Former.—Considerably in excess of two molecules of hydrazine hydrochloride were allowed to act on one molecule of resodiacetophenone on the steam-bath under a reflux condenser in a 1:1 aqueous alcoholic solution to which sodium acetate in an amount equivalent to the hydrochloride had been added. The heavy, yellow precipitate which formed was collected on a filter and washed first with hot water and then with alcohol and dried by suction and plating. This derivative, although soluble in alkalies, is highly insoluble in the common low-boiling organic solvents, but is soluble in hot nitrobenzene or aniline; with the latter, however, a further condensation takes place, as described below. Purification by dissolving in ten per cent. sodium hydroxide and precipitation by hydrochloric acid gave a compound which does not melt under 300° but which changed from yellow to light red between 240° and 260°, and back again to the yellow modification on cooling. Analysis shows that it is monazine of resodiacetophenone, in which one molecule of hydrazine has condensed with two molecules of the ketone:



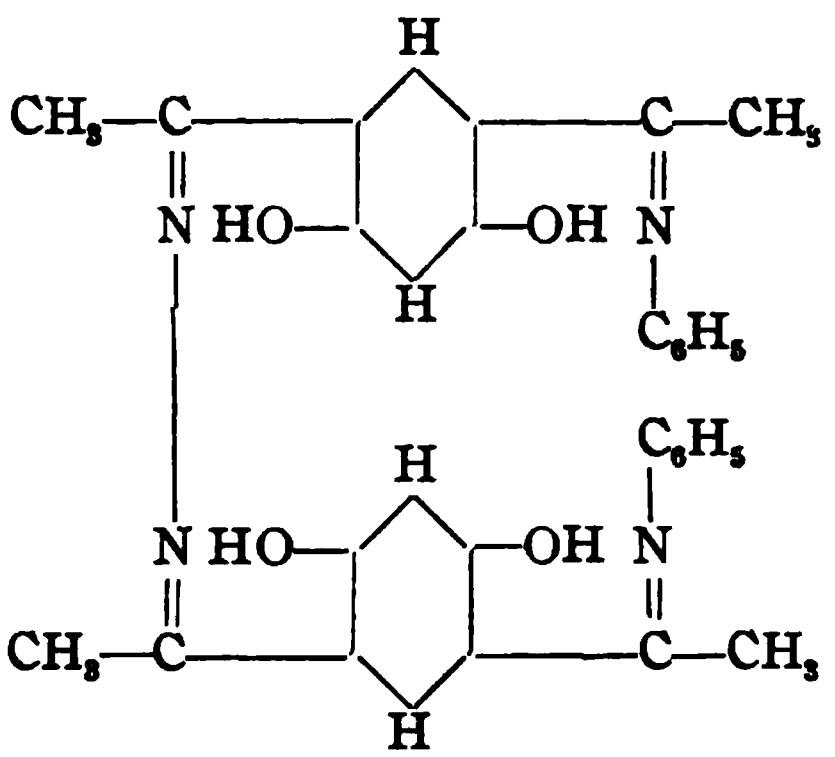
Calculated for $C_{10}H_{20}O_6N_2$: N, 7.29.
Found: N, 7.07.

By carrying out the reaction between hydrazine hydrochloride and resodiacetophenone with a solution of sodium hydroxide instead of sodium acetate, complete condensation between two molecules of hydrazine and two molecules of resodiacetophenone takes place. When sodium acetate is used, the marked insolubility of the first condensation product probably prevents any further reaction. In the reaction in alkaline solution a ten per cent. aqueous sodium hydroxide was used at the temperature of the steam-bath, the alkali-soluble azine compound was precipitated out with hydrochloric acid and dried by plating and suction. The solubilities were found to be about the same as for the monoazine derivative. At 150° the red modification begins to appear, and is much deeper in hue. A small amount kept between this temperature and 300° for about twenty minutes, and then allowed to cool, returns again to the yellow form. On heating in a mixture of acetic and hydrochloric acids, both azine derivatives are decomposed; resodiacetophenone was recovered from the solutions by diluting with water. Analyses of the compound gave results which correspond with the following formula, a bisazine of resodiacetophenone:



Calculated for $C_{20}H_{20}O_4N_4$: N, 14.73.
Found: N, 14.48, 14.43.

On heating the monazine with aniline, further condensation takes place, *viz.*, between two molecules of aniline and the two free carbonyl groups, giving a dianilido monazine of resodiacetophenone, which is insoluble in aqueous alkalies.



Calculated for $C_{22}H_{20}O_4N_4$: N, 10.48; C, 71.91; H, 5.62.
Found: N, 10.97, 10.65, 10.66; C, 71.74; H, 4.54.

Action of Bromine on Resodiacetophenone.—The direct action of bromine on acetophenone[1] gives the ω-bromaceto derivatives, while in the action of bromine on paeonol acetate in carbon disulphide, some of the bromine goes into the side chain, giving exo-brompaeonol acetate, $C_6H_2(OCH_3)_2OCOCH_3COCH_2Br$, and at the same time esobrompaeonol, $OHC_6H_2BrOCH_3COCH_3$, is formed by the action of bromine on the paeonol formed by saponification of the acetate by hydrobromic acid.[2] In studying the action of bromine on resodiacetophenone, we found difficulty in obtaining satisfactory results, since by no variation of the method of preparation or purification could a compound of sharp melting-point be obtained. We have, however, obtained a monobrom derivative in a fair degree of purity and this seems pretty certain to be a ring and not a side-chain substitution product. One molecule of bromine was added to one of resodiacetophenone and the mixture was allowed to stand for six or eight hours with occasional stirring until hydrobromic acid ceased to be evolved. A white, crystalline product was obtained which, after numerous crystallizations from chloroform and alcohol, failed to give a sharp melting-point, gradual liquefaction taking place between 197–202°. Analysis, however, gave a satisfactory result for a monobrom derivative.

Calculated for $C_{10}H_9O_4Br$: Br, 29.31.
Found: Br, 29.38.

Some of the product was allowed to stand with a ten per cent. sodium hydroxide solution for several hours and was finally thrown out of solution with hydrochloric acid. The precipitate had a light yellow color, which crystallization from chloroform did not change and the melting-point was still not sharp, 200–3°. Analysis showed that practically

[1] *Ber.*, 10, 2006.
[2] *Ibid.*, 30, 299.

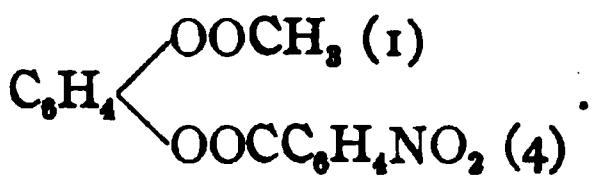
no bromine had been removed by this treatment, which points to substitution in the ring rather than in the side chain. Found, 28.80 per cent. bromine. When the bromination was carried on in chloroform or when several molecules of bromine were used, the products contained large quantities of bromine, much of which could be removed by treatment with alkalies. The products obtained by bromination had a very strong action on the mucous membrane. On treatment with potassium hydroxide, this action was entirely destroyed.

Bromresodiacetophenone Bisphenylhydrazone, $C_6HBr(OH)_2(C:CH_3N_2HC_6H_5)_2$.—About two molecules of phenylhydrazine were added to one molecule of the monobrom resodiacetophenone dissolved in hot alcohol. On standing for a few hours, the bisphenylhydrazone separated out in beautiful light yellow crystals, slightly soluble in hot benzene and toluene and almost insoluble in alcohol and ether. Crystallized from chloroform, the compound decomposes at 215–20°. It is insoluble in ten per cent. sodium hydroxide in the cold; on heating it dissolves with saponification of a phenylhydrazine group, made evident by the odor of free phenylhydrazine. The phenylhydrazone of the bromresodiacetophenone which had been treated with alkali was also made and the same light yellow product was obtained.

Calculated for $C_{22}H_{22}O_2N_4Br$:	Br, 17.66.
Found:	Br, 17.86.

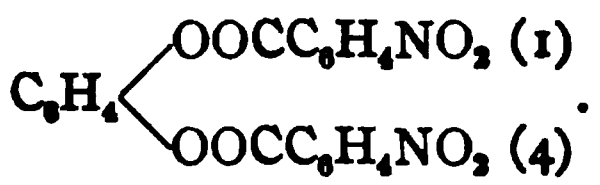
In connection with our work on the dihydroxybenzophenones, we attempted to obtain nitro derivatives by the action of acid chlorides of the nitrobenzoic acids on the acetate, benzoate, nitrobenzoate, and methyl ether of hydroquinone in the presence of various catalyzing agents, as the chlorides of aluminum, zinc or copper. In no case, however, did we obtain benzophenones, but with the acetates found that one or more of the acetyl groups had been replaced by nitrobenzoyl groups. Thus the action of two molecules of nitrobenzoyl chloride on one molecule of hydroquinone diacetate in the presence of anhydrous aluminium chloride at 130–140° gave, besides a small amount of unchanged nitrobenzoyl chloride, two compounds which were readily separated from each other by their different solubilities. After allowing the reaction to proceed for about two hours with occasional additions of aluminium chloride, the reaction product was treated with very dilute hydrochloric acid and finally with a little ammonia to free it from nitrobenzoic acid. After drying on a porous plate, the portion soluble in alcohol was extracted and crystallized from this solvent, in which it is quite soluble when hot and somewhat less so in the cold; its solubility in benzene is similar. The melting-point was 113°. It is insoluble in cold aqueous alkalies, but dissolves rather rapidly on heating. Analysis shows that the compound is hydroquinone

monoacetatemononitrobenzoate, one acetyl derivative having been replaced by the nitrobenzoyl group,



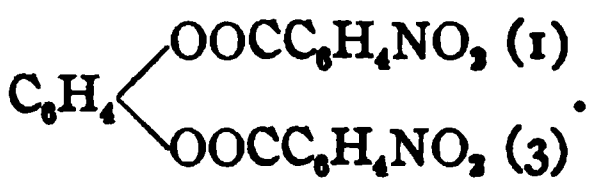
Calculated for $C_{15}H_{11}O_6N$: C, 59.80; H, 3.65; N, 4.65.
Found: C, 59.18; H, 4.02; N, 4.63.

That portion of the product insoluble in alcohol was found to be insoluble also in most of the common organic solvents. It was found possible, however, to crystallize it from hot acetic anhydride, from which it is deposited in small white needles. It is very soluble in hot nitrobenzene and but slightly so in the cold solvent; it is somewhat less soluble in hot diethyl oxalate than in hot nitrobenzene. The melting-point was 268°. Condensation of two molecules of *m*-nitrobenzoyl chloride or the free acid and one of hydroquinone in the presence of phosphorus oxychloride gave the same compound. It is slowly saponified by alcoholic potash, giving some *m*-nitrobenzoic acid. The method of preparation, the saponification product and the analyses show the compound to be hydroquinone-*m*-nitrodibenzoate,



Calculated for $C_{20}H_{12}O_8N_2$: C, 58.82; H, 2.94; N, 6.86.
Found: C, 58.63; H, 4.19; N, 6.62.

Resorcinol *m*-nitrodibenzoate was formed in a similar attempt to prepare the benzophenone, and likewise by the direct action of *m*-nitrobenzoyl chloride on resorcinol. In this case mere heating on the steam-bath for a few hours gave a completed reaction, while with hydroquinonol a temperature of 130° was required. The solubilities are similar to those of the analogous hydroquinonol derivative. It was crystallized from nitrobenzene, m. p. 172°. Analysis gave results for resorcinol *m*-nitrodibenzoate,

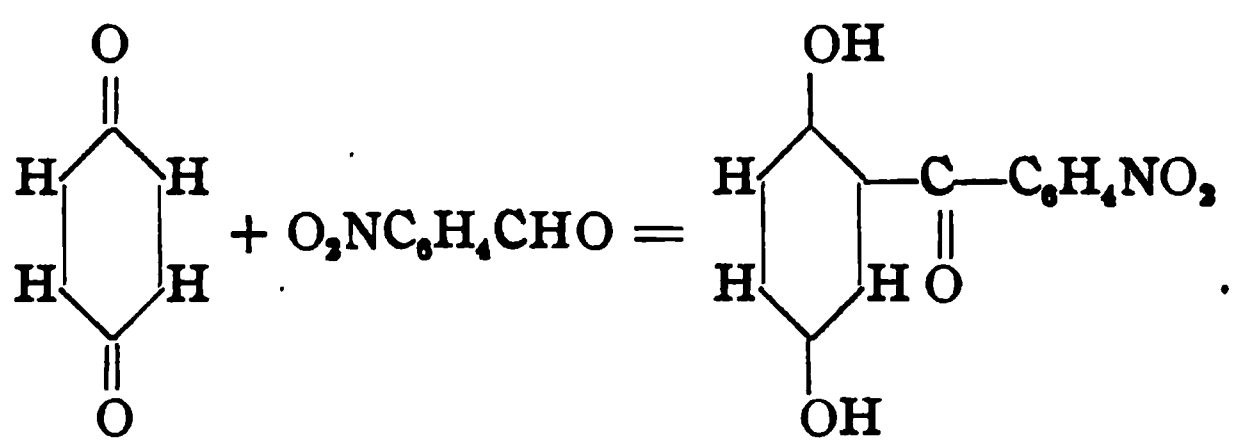


Calculated for $C_{20}H_{12}O_8N_2$: C, 58.82; H, 2.94; N, 6.86.
Found: C, 58.47; H, 3.27; N, 6.69.

The action of *m*-nitrobenzoyl chloride on resorcinol dibenzoate in a number of different solvents such as carbon disulphide, phosphorus trichloride and phosphorus oxychloride was tried without result. Orthonitrobenzoyl chloride on resorcinol dibenzoate in the presence of anhydrous zinc chloride and infusorial earth gave entirely unsatisfactory results, while *o*- and *m*-nitrobenzoyl chlorides on resorcinol or hydroqui-

nonol *m*-nitrobenzoate in the presence of various catalyzers, as anhydrous zinc and aluminum chlorides and metallic copper gave no reaction. The dimethyl ether of resorcinol is a derivative in which the substituting groups are comparatively stable and should offer little interference; with *o*-nitrobenzoyl chloride and zinc or aluminum chlorides, however, the acid chloride was decomposed and with *m*-nitrobenzoyl chloride, although hydrochloric acid was given off, it was found that the reaction consisted principally in the replacement of the methyl by the nitrobenzoyl groups. This reaction is in line with the observation of A. Claus[1] that acetyl chloride in the presence of zinc chloride tends to remove the methyl groups in the methyl ether of resorcinol. Since an excellent method for preparing resodiacetophenone is the isomerization of resorcinoldiacetate by means of zinc chloride, an attempt was made to isomerize the resorcinol-*m*-nitrobenzoate; with anhydrous zinc chloride at 130–140° there was no change, and with mixtures of zinc chloride and aluminum chloride or with aluminum chloride alone, carbonization occurred before the desired reaction took place.

Since acetaldehyde[2] and benzaldehyde,[3] acting on quinone, give, beside the acetate and benzoate and quinhydrone, considerable quantities of the dihydroxy aceto- or benzophenone, it was thought possible that the nitrobenzaldehydes might react in a similar way upon quinone, yielding dihydroxynitrobenzophenones:



Accordingly, quinone was dissolved in melted *o*-nitrobenzaldehyde and allowed to stand in the sunlight for several weeks, but no condensation took place, the nitrobenzaldehyde having been isomerized simply to nitrosobenzoic acid, a reaction which G. Ciamician and P. Silber[4] have shown takes place with the former substance under the influence of sunlight. Salicylaldehyde, in the sunlight, acted as a reducing agent on quinone, giving quinhydrone and salicylic acid. The study of alkali-insoluble phenols is being continued in this laboratory.

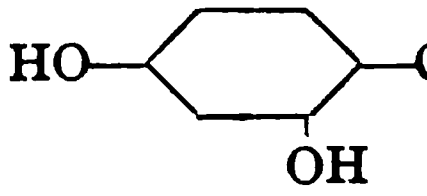
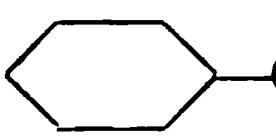
[1] *J. pr. Chem.* [2], 53, 39.
[2] *Ber.*, 31, 1214.
[3] *Ibid.*, 24, 1341.
[4] *Ibid.*, 34, 2040.

CAMBRIDGE, MASS.

THE ACTION OF PHTHALIC ANHYDRIDE ON RESACETOPHENONE.

By Henry A. Torrey and C. M. Brewster.

Received March 13, 1908.

In the preceding paper by H. B. Kipper and one of us we have called attention to the replacement of the acetyl group by the nitrobenzoyl group in resorcinol diacetate and hydroquinonol diacetate. In the present article we wish to record a more remarkable reaction in which the acetyl group in resacetophenone,  , a compound in which that radical is directly attached to the ring, has been replaced by a group of higher molecular weight. By heating two molecules of resacetophenone and one molecule of phthalic anhydride with a dehydrating agent, such as anhydrous zinc chloride, sulphuric acid, or phosphoric acid, then acetic acid is given off and fluoresceïn is formed in large amount. It has been known for a long time that acetophenone, heated with concentrated sulphuric acid, gives benzoic acid and benzenesulphonic acid[1] and Hoogewerf and van Dorp[2] have shown that in substituted aromatic methyl ketones carrying a methyl group in the ortho position to the acetyl group, sulphuric acid has the power of replacing the ketone radical by hydrogen, while Klages[3] had found somewhat earlier that although the aromatic ketones of the type  —COR were unaffected by heating with phosphoric acid, those ketones in which an alkyl group is in the ortho position may be changed into the corresponding hydrocarbon; the decomposition takes place most easily with diortho alkyl derivatives. The formation of fluoresceïn from resacetophenone and phthalic anhydride does not seem to be due to the formation of resorcinol by the splitting out of the acetyl group which then reacts with the phthalic anhydride, for when resacetophenone was heated with concentrated sulphuric acid no odor of acetic acid was noticed.

The procedure in this method for preparing fluoresceïn was as follows: The mixture of 20 grams of resacetophenone and 10 grams of phthalic anhydride, after slightly moistening with water and adding 5 grams of concentrated sulphuric acid, was heated with constant stirring until melted. The rate of condensation was watched by dissolving small portions in sodium hydroxide and observing the color and quality of the precipitate obtained on acidification. When a large yield of a bright

[1] Krekeler, *Ber.*, 19, 678.

[2] *Koninklijke Akad. van Wetenschappen te Amsterdam*, 1901, 173. *Chem. Centr.*, 72 [2], 1117.

[3] *Ber.*, 32, 1549.

yellow precipitate was secured, the reaction was stopped and the mixture poured into a large quantity of cold water, when the fluoresceïn separates out in a bright yellow, flocculent mass; if a dark precipitate is obtained, the mixture has been heated too long. The fluoresceïn may then be purified by fractional precipitation from an alkaline solution with acid, which gradually removes a tarry impurity probably containing resaceteïn. Another method of purification consists in dissolving the crude fluoresceïn in concentrated sulphuric acid diluted with an equal volume of water and precipitating after filtration by neutralization with sodium hydroxide. That acetic acid is actually given off in the reaction was shown by the odor, by the ferric chloride and the ethyl acetate tests. That the compound formed was actually fluoresceïn was shown by conversion into the diacetate, the dichloride and eosine. The diacetate made either by heating with acetic anhydride or by acetylation with acetyl chloride and pyridine in glacial acetic acid, after purification by crystallization from acetone, melted at 201°, while Baeyer[1] gives 200°.

Calculated for $C_{24}H_{16}O_7$:	C, 69.23; H, 3.88.
Found:	C, 69.04, 69.24; H, 4.03, 4.09.

From this diacetate fluoresceïn was obtained by saponification. The dichloride was made by heating with phosphorus pentachloride at 180°. After crystallization from alcohol it gave a melting-point of 249° (Baeyer, 252°). Calculated for $C_{20}H_{10}O_3Cl_2$: Cl, 19.22; Found, 19.20.

Eosine was made by adding bromine to an alcoholic solution of the fluoresceïn. Calculated for $C_{20}H_8O_5Br$: Br, 49.36; Found, 48.76. Succinyl fluoresceïn was formed with elimination of acetic acid when the condensation was carried on with succinic acid instead of phthalic anhydride.

THE OPTICAL ROTATION OF SPIRITS OF TURPENTINE.

By Chas. H. Herty.

Received February 10, 1908.

Among the physical properties of spirits of turpentine, none has proved of more interest than its optical rotation. In most specimens this property is very marked, and as the liquid is colorless and the determination readily made, many data are found on this subject in chemical literature. Slight variations in the rotation of different samples are to be expected, as spirits of turpentine is not a chemical compound but a mixture of substances, chiefly terpenes. From the results of numerous observations upon commercial samples, the view commonly held previous to 1891 was that French spirits of turpentine, distilled from the oleoresin of *Pinus maritima*, is levo-rotatory and that American spirits of turpen-

[1] *Ann.*, 183, 1.

tine, distilled in years past, almost wholly from *Pinus palustris*, is dextro-rotatory. The difference in the character of the rotation was ascribed, therefore, to the different species from which the spirits of turpentine was produced.

Recognizing the fact that American spirits of turpentine is distilled from more than one species of pine, J. H. Long,[1] in 1891, undertook a study of the volatile oils distilled from oleoresins of well identified individual trees, these trees embracing the several species of pines subjected to turpentining in our southern states. He found that specimens from *Pinus palustris* (Long Leaf Pine)gave dextro-rotatory oils, while those from *Pinus heterophylla* (Cuban or Slash Pine) gave levo-rotatory oils. Since the oleoresins from these two species are indiscriminately mixed, at the time of collection in the woods, the rotation of the oil distilled from such a mixture would naturally vary. *Pinus palustris* is the predominating species and Long attributed to this fact the dextro-rotatory character of American spirits of turpentine. This view has been generally accepted.

The fact that spirits of turpentine is frequently adulterated with optically inactive mineral oil, led A. McGill[2] to make a large number of determinations of the rotation of commercial samples of spirits of turpentine, in the hope of utilizing this property for the detection of adulteration. From the widely varying results obtained he was compelled to declare the method useless.

New evidence upon this point has been obtained from investigations carried on in this laboratory in collaboration with the U. S. Forest Service, the experimental work having been carried out by Messrs. George A. Johnston and W. S. Dickson under the direction of the writer. In order to gain a better knowledge of the oleoresins from the two principal species of pine utilized in the turpentine industry at the present time, fourteen trees were selected on a Florida turpentine farm. One-half of these were *Pinus palustris*, the other half *Pinus heterophylla*. Three trees of each species were tapped for the first time at the beginning of the experiments. In each case a small, young pine, a medium pine, and a large, old pine were selected. In another set four trees were selected, two each *Pinus palustris* and *Pinus heterophylla*. These trees had been subjected to turpentining during the previous year, the chipping, or weekly scarification, on all of them having been unusually shallow, only about one-half as deep as is commonly practiced. In a third set four trees were selected, two each of *Pinus palustris* and *Pinus heterophylla*, which had been turpentined during the previous year, and on each of these the depth of the chipping was the normal cut. The trees in each set were chipped at intervals of seven days.

[1] *J. Anal. Appl. Chem.*, 6, 1.

[2] *Bulletin No.* 79, *Inland Revenue Dept., Canada.*

Special precautions were taken in the collection of the oleoresins. The cup and gutter system described in *Bulletin No. 40, U. S. Bureau of Forestry*, was used. Instead of the clay cup commonly used, oyster pails were substituted. The entire apparatus was covered with black oil-cloth fastened securely into the bark of the tree above the chipping surface, thereby protecting the resin from light and avoiding the filling of the pails with rain water. Every four weeks these pails were removed from the tree, tightly stoppered and immediately shipped to this laboratory for examination. The specimens so obtained were extremely pure and free from chips. After removal of the pails, the metal gutters were raised to a point near the chipping surface in order to minimize the amount of oleoresin which might stick to the exposed portion of the trunk above the gutters.

The distillation of the oleoresin was carried out in a 500 cc. Kjeldahl flask, surrounded by a bath of cottonseed oil. Steam from a small boiler was first passed through a small iron pipe in which it could be superheated, then into the distillation flask through a glass tube having on its end a bulb containing a number of openings. By this means strong agitation of the molten oleoresin was obtained. Thermometers were placed both inside the flask and in the oil-bath. The mixed vapors of steam and spirits of turpentine were passed through a Hopkins condensing bulb to prevent the carrying over of solid particles of resin, condensed in an ordinary Liebig condenser and collected in a separatory funnel. After drawing off the lower layer of water, the spirits of turpentine was transferred to a dry flask and allowed to stand over night with calcium chloride. The determinations of the optical rotation of the volatile oils were made with a Schmidt and Haensch half-shadow polariscope, sodium flame, at 20°.

In the following table are given the results from the first collection of the oleoresin in early spring:

TABLE I.

Tree designation.	Species.	Diameter (inches).	Character of chipping.	Optical rotation 100 mm. tube, 20° C.
A1	*P. heterophylla*	7.0	1st year, normal depth	—20°50′
A2	"	14.5	" "	+ 0°15′
A3	"	24.5	" "	—15° 0′
A4	*P. palustris*	7.3	" "	+15°40′
A5	"	15.0	" "	+ 8° 9′
A6	"	21.0	" "	+18°18′
C1	*P. heterophylla*	12.3	2nd year, shallow	—27°11′
C2	"	8.2	" "	—26°28′
C3	*P. palustris*	13.0	" "	— 7°26′
C4	"	8.7	" "	+ 7°31′
D1	"	9.0	2nd year, normal depth	+10°50′
D2	"	13.5	" "	+ 1°23′
D3	*P. heterophylla*	13.0	" "	—18°35′
D4	"	9.0	" "	—29°26′

These results show a wide variation in the optical rotation of the volatile oils from the individual trees, even among trees of the same species. In a general way the figures give support to Long's view, namely that the volatile oils from the *Pinus palustris* are dextro-rotatory and those from *Pinus heterophylla* levo-rotatory. That this is not strictly true, however, is evidenced by the dextro-rotation of A2 (*P. heterophylla*) and more especially by the levo-rotation of C3 (*P. palustris*).

With these variations in the first collection from the several trees, the question naturally arose, would the variations change as the season advanced or would the figures prove constant for the individual trees? The rotations for the successive collections follow in Table II:

TABLE II.—OPTICAL ROTATION IN 100 MM. TUBE, 20° C.

Collection.	A1.	A2.	A3.	A4.	A5.	A6.	C1.
1..	—20°50′	+0°15′	—15° 0′	+15°40′	+8° 9′	+18°18′	—27°11′
2..	—22° 5′	—0°30′	—14°26′	+15°22′	+8°50′	+17°43′	—26°48′
3..	—21°45′	+0°15′	—15°55′	+14°15′	+8°27′	+19°30′	—26°25′
4..	—21° 7′	—1°15′	—15°50′	+14°20′	+8°34′	+18°46′	—23°32′
5..	—20°30′	—2° 5′	—15°15′	+14°21′	+8°32′	+19°24′	—21°12′
6..	—20°15′	—3°30′	—15°27′	+14°35′	+8° 4′	+18°16′	—21°46′
7..	—22°15′	—5°45′	—17°52′	+12°49′	+7° 6′	+14°47′	—21°35′

Collection.	C2.	C3.	C4.	D1.	D2.	D3.	D4.
1..	—26°28′	—7°26′	+7°31′	+10°50′	+1°23′	—18°35′	—29°26′
2..	—25°37′	—6°42′	+7°20′	+11°23′	+2°40′	—17° 0′	—27°45′
3..	—26°20′	—4°45′	.....	+13° 7′	+2°25′	—15°20′	—28°19′
4..	—26°30′	—4°29′	.....	+12°46′	+2°25′	—15° 0′	—27°38′
5..	—26° 7′	—3°55′	.....	+13° 0′	+1°13′	—14°38′	—27°48′
6..	—26° 0′	—4° 5′	.....	+13° 0′	+1°15′	—14° 7′	—26°11′
7..	—26°28′	—6° 6′	.....	+10°48′	—0°55′	—14°19′	—26°12′

NOTE.—The yield of oleoresin from C_4 was so small, after the first and second collections, that not enough volatile oil could be obtained on distillation to fill the 100 mm. tube.

From this table it is seen that the rotation in most cases is quite constant throughout the year. The most marked exception is A2 (*P. heterophylla*). It is evident that some distinct change in the biological activity of this tree has taken place, for while the rotation is reasonably constant during the first half of the year, a steady increase in the levo-character of the oil is apparent during the last half. In the case of C1 (likewise *P. heterophylla*) somewhat the reverse has taken place. A rather marked decrease in the levo-rotation is shown just at the middle of the year, then the rotation remains practically constant during the last half. In the case of C3, another type of change is represented, the levo-rotation decreasing up to the middle of the season and again increasing during the latter half.

With the limited facts at hand, it is impossible to interpret the signifi-

cance of these changes. That tree which shows the most marked variation, A2, is a healthy, vigorous tree, from which variations would be least expected. Nor can an explanation be offered for the wide variations in the optical rotation of oils from the same species. All of the trees in Series A are located within 20 yards of each other and have, therefore, the same general conditions of climate, light and soil. Fractionation of the volatile oils from these show practically the same rise in boiling-point for the same volume of distillate. It would seem, therefore, that these volatile oils, consisting so largely of pinene, are mixtures principally of dextro- and levo-pinene, the preponderance of the one or the other determining the optical rotation.

UNIVERSITY OF NORTH CAROLINA,
CHAPEL HILL, N. C., February 2, 1908.

A METHOD OF ANALYZING SHELLAC.[1]

BY PARKER C. MCILHINEY.

Received March 13, 1908.

The method of analysis which is in most common use at the present time, both in England and in the U. S., for the determination of the amount of rosin in shellac, is an indirect method depending upon the different powers of a shellac and of rosin to absorb iodine from a suitable solution. Different operators prefer different methods of making this test, some preferring to use the old Hubl method, and others the more modern Wijs method, as modified by Langmuir. Either of these methods is capable of giving reasonably satisfactory results, although the Langmuir method is certainly much to be preferred, both on the score of accuracy and of speed. Another method which is in use is that proposed by Parry, depending upon the solubility of the resinate of silver made from common rosin, in ether, while the corresponding resinates from shellac are insoluble. This method labors under several disadvantages and sources of error, of which the two principal ones are the solubility of the unsaponified portion of the shellac in ether, and the danger of a decomposition of the resinate of silver before it can be separated and determined.

A direct method of separating shellac and rosin and recovering the rosin, at least, in a substantially unchanged form, is greatly to be desired, and several experimenters have attempted to make such a separation by taking advantage of the solubility of rosin in petroleum ether, a solvent in which shellac is insoluble. No method of extracting from even a finely pulverized sample of shellac the portion soluble in petroleum ether seems to be capable of removing more than a small part of the rosin contained in the sample.

[1] Read before the New York Section on March 6, 1908.

Shellac dissolves in alcohol, except for the wax contained in it; petroleum ether dissolves to some extent in alcohol and it was thought that by first dissolving the shellac to be analyzed in alcohol, then adding to the solution all the petroleum ether which it would dissolve, and then adding water, so as to so dilute the alcohol that it would no longer have any material solvent power upon either rosin or shellac, there should result a separation of the dissolved petrolic ether containing in solution the rosin and the wax, but free from the resinous constituents of the shellac. Upon trying this process, it appeared that it was correct in principle, but that on account of the limited solubility of petroleum ether in alcohol, the separation was not quite complete. Upon substituting for ordinary alcohol, glacial acetic acid, or absolute alcohol, in which the sample of shellac to be examined is dissolved and then adding to it petroleum ether, which is miscible in all proportions with acetic acid, or absolute alcohol, it was found practicable to combine with the rosin and the wax so large an amount of petroleum ether, that upon adding water, an almost complete separation of the rosin and wax from the resinous part of the shellac could be effected.

Based upon these facts, the following process was devised: Dissolve in 20 cc. of glacial acetic acid (about 99 per cent.), or the same volume of absolute alcohol, 2 grams of the sample to be analyzed. This requires a gentle heat. Add to the solution, after cooling, 100 to 300 cc. of petroleum ether, boiling under 80°. This addition of petroleum ether should be made slowly, because the addition of so large an amount of petroleum ether precipitates from its solution a part of the shellac, combined, apparently, in case acetic acid was the original solvent, with acetic acid to form a liquid precipitate. It is manifestly desirable that this precipitation of part of the shellac should not be effected by too sudden an addition of petroleum ether, as it might then contain some rosin carried down mechanically with it.

We now have a solution containing both petroleum ether and glacial acetic acid, or absolute alcohol, and containing in it, in solution, all the rosin, all the wax and most of the resinous part of the shellac. Add now to this solution, drop by drop, 100 cc. of water, agitating the liquid during the addition. The water "unites with" the alcohol or acetic acid, and separates from the liquid the petroleum ether with whatever is soluble in petrolic ether. This includes the rosin and the wax. The shellac is also precipitated, but as it is insoluble in petroleum ether it remains as a precipitate suspended in the diluted alcohol or acetic acid. The separation of the two liquids takes place very rapidly, and it is an easy matter to effect a complete separation of the two layers in a separating funnel. The petroleum ether layer is washed once or twice with water and then filtered through a dry paper into a weighed flask, from which the petroleum

ether is then distilled off, leaving the residue of rosin mixed with wax, which is weighed. To the weighed residue neutral alcohol is added, and the flask heated to dissolve the rosin in the alcohol. The liquid is then titrated with N/5 or N/10 caustic potash. This gives a measure of the amount of rosin present, as the average combining equivalent of rosin does not vary greatly from 346. This is the figure used for this titration in the Twitchell process. It is much better, however, not to depend upon his determination of the rosin but to proceed to an actual separation by adding to the neutralized alcoholic solution, a distinct excess of alkali, and a sufficient quantity of petroleum ether; the mixture is then transferred to a separating funnel, thoroughly agitated, and some water added. The liquids are then separated, the petroleum ether layer being washed with water, and the alcoholic solution of the rosin extracted once more with petroleum ether. The petroleum ether solutions are then united, the petroleum ether distilled off, and the residue of wax weighed. The alcoholic solution containing the rosin is then boiled until the alcohol has been expelled, and, if necessary, a further addition of water made; then dilute hydrochloric acid is added, so as to precipitate the rosin. This should be done in a weighed flask; the acidified liquid can now be decanted off through a wet filter paper so as to leave behind in the flask the major part af the rosin, which is washed with water. The remainder of the rosin upon the filter paper after sufficient washing, is extracted with petroleum ether back into the weighed flask from which the water has been decanted as perfectly as possible. Upon distilling off the petroleum ether, the rosin is left behind in a condition to weigh. If the whole of the last traces of water have not been removed by the distillation with petroleum ether, it is well to add a further quantity of dry petroleum ether and distil again.

Attempts were made to use other solvents, particularly coal tar benzene instead of petroleum ether. It was found, however, that benzene dissolved considerably more out of the shellac than the wax.

If it is desired to determine only the rosin in the shellac, it is unnecessary to distil off all the petroleum ether from the solution containing the wax and the rosin. This solution may, instead, be treated directly with an alkali capable of combining with the rosin, while leaving the wax unattached. The most convenient method which I have found for accomplishing this is to add to the petroleum ether solution, after filtering it to remove from it anything which it may contain in suspension, a solution of sodium hydroxide in absolute alcohol. Such a solution I have found it convenient to make by dissolving in ordinary 95 per cent. alcohol the appropriate amount of metallic sodium. Such a solution, when added to the petroleum ether solution, mixes perfectly with it, and the alkali combines with the rosin, and the mixed solution allows the saponified

rosin to be extracted from it by agitation with water, or better, with slightly diluted alcohol. Instead of using a solution of sodium hydroxide in absolute alcohol, it should be possible to use the method of separating rosin from neutral substances in petroleum ether solution, that is used in the Twitchell process of determining rosin in admixture with fatty acid. This consists in agitating the petroleum ether solution with an alkaline aqueous solution, containing some alcohol, made by dissolving one gram of potassium hydroxide with 10 cc. of alcohol in water, and diluting to 100 cc. I have found the other method of procedure advantageous, however, and believe it to give a more exact separation. The solution drawn off from the petroleum ether, after extraction by alkali and containing in solution the rosin, combined with potassium or sodium, together with whatever alcohol has been used to promote the combination and to facilitate the mechanical separation of the two liquids, is heated for some time to remove the alcohol, and is then acidified with hydrochloric or with sulphuric acid to precipitate the rosin. The precipitated rosin is then weighed as before.

Without entering into a discussion of the exact chemical composition of shellac wax, it may be proper to state that the wax may be separated commercially from shellac by two essentially different methods, which will probably give waxes having somewhat different compositions. If the shellac is dissolved in an alkaline solution and the wax which remains in suspension is filtered out, it is probable that different results will be obtained from what would be obtained by the other process, consisting of a solution of the shellac in alcohol, and filtration of the solution to remove the wax which will then remain in suspension. It is to be expected that these two processes of solution would leave, in the undissolved wax, small amounts of ingredients of different characters, and, furthermore, the alcohol used in the second process would dissolve small amounts of the wax which would probably be quite insoluble in an alkaline aqueous solution. Again, it is quite probable that a caustic solution would behave towards shellac wax somewhat differently from a dilute carbonate solution. For the sake of uniformity and simplicity, I am assuming that shellac wax is quite free, when pure, from all acid substances capable of uniting with free alkali. It is, nevertheless, true that the user of shellac who wishes to have a determination made of the amount of wax which it contains, usually desires this information in order that he may know how much of the shellac will remain undissolved in alcohol. This amount of insoluble wax will, of course, vary to some extent, depending upon the strength of the varnish that he prepares with it, that is to say, the number of pounds of shellac which he uses to a gallon of alcohol. As the analyst can hardly be expected to take account of this in making his test, it appears more rational to regard as

wax the whole of those matters contained in the shellac that remain insoluble in an alkaline solution.

In making a determination of the amount of wax in a sample of shellac, by this method, it is to be observed that some constituent of shellac wax is evidently only difficultly soluble in petroleum ether. Upon submitting several portions of the same lot of shellac to analysis in this way, the only difference made in the different determinations being that varying amounts of petroleum ether were used, the series of analyses gave, with increasing amounts of petroleum ether, increasing percentages of wax, until the proportion of about 125 to 150 cc. of the solvent to 1 gram of a shellac containing about 5 per cent. of wax was reached. It may be that by using some other solvent such as benzene for the determination of wax in this way, a smaller amount will suffice, but as it seldom happens that only wax without rosin is to be determined, petroleum ether is the most generally applicable solvent. The solubility of rosin in petroleum ether is so easy and complete that no difficulty is experienced in extracting from 2 grams of shellac 50 per cent. of rosin, using 100 cc. of petroleum ether.

Whenever in the course of an analysis by this method a quantity of material is separated by acidifying the aqueous solution which should contain the rosin, its identity may be established with some certainty by determining its iodine figure by the Langmuir method, and its acidity by titrating with alkali in alcoholic solution.

The petroleum ether referred to here is a solvent made by redistilling 71° Bé. benzine, separating for use that part which distils below 80°. This fraction constitutes a large proportion of 71° benzine, and such a redistillation gives, at a comparatively small cost, a satisfactory solvent for the purpose. If a determination of only the rosin is desired, it is of course unnecessary to be very particular as to the volatility of the solvent used, as it is unnecessary in such case to distil it off before extracting the rosin by alkali.

By treating pure shellac according to this process, it is possible to separate from it a small amount, sometimes as much as 1 per cent., of materials soluble in petroleum ether. This small amount of resinous matter, when examined, proves to be something essentially different from common rosin. Its odor and its low iodine figure indicate that it is some resinous constituent of shellac, perhaps a small amount of the major constituent, which is slightly soluble in petroleum ether. As it is difficult to imagine that by this process rosin if a normal constituent of pure shellac would escape detection, and as the small amount of resinous matter here obtained is essentially different from rosin, it is reasonable to conclude that, contrary to the idea held by many, common rosin or a material similar to it, is not a natural constituent of pure shellac, but

that any rosin or colophony, which can be separated in a state of reasonable purity from the sample of shellac, was originally added to the shellac, as an adulterant.

The process here described allows the analyst to separate in a form convenient for exhibition either as evidence in court or as an ocular demonstration for his client, any rosin which may have been added as an adulterant to shellac.

Shellac varnishes may contain beside true shellac not only rosin, but other gums and resins soluble in alcohol. It becomes, therefore, a matter of interest to ascertain how some of these other resins behave when treated by this process. Two samples of manilla, when treated, using absolute alcohol as the first solvent, gave respectively, 41.2 and 43.3 per cent. of matter soluble in petroleum ether. The acidity of these two lots of matter soluble in petroleum ether was in the case of the first sample such that 1 cc. of normal alkali neutralized 411.7 milligrams and in the case of the second 470.7 milligrams. Two samples of Kauri gave, respectively, 37.9 and 27.0 per cent. Upon titrating with standard alkali these portions soluble in petroleum ether, it appeared that 1 cc. of normal alkali was capable of neutralizing 903.6 mg. and 742.5 mg., respectively. Of Sandarac, two samples, when similarly analyzed, gave 34.96 and 36.19 per cent., having such an acidity that of the first 541.2 mg. would neutralize 1 cc. normal alkali, and of the second, 552.5 mg. would neutralize 1 cc. Of Dammar, 89.9 per cent. proved to be soluble, while the resin of *Shorea roburta*, a sample of which was kindly sent by Mr. W. Risdon Criper, of Calcutta, gave 69.5 per cent. of soluble matter.

A number of attempts were made to effect a satisfactory separation of the wax before separating the rosin from the shellac. It was found, however, that on account of the solubility of wax in alcohol and in glacial acetic acid, this separation could not well be made by filtering out the wax before the addition of petroleum ether. Neither were attempts which were made to separate the wax by a preliminary solution of the shellac in aqueous alkali successful in furnishing a method that at all approached in feasibility to the method already described.

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THE VOLATILE OIL OF PINUS SEROTINA.

BY CHAS. H. HERTY AND W. S. DICKSON.

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Scattered among the forests of Long Leaf pine along the Atlantic seaboard, there are found, usually in mixed stands, patches of Pond pine (*Pinus serotina*) and Loblolly pine (*Pinus taeda*). These pines are seldom subjected to turpentining, as the yield of oleoresin is not so plenti-

ful as from the predominating types *Pinus palustris* and *Pinus heterophylla*. Nor are the two species usually distinguished locally, the name "black pine" being applied to each. The striking odor of the wood of *Pinus serotina* when freshly cut made desirable an investigation of its volatile oil, and in collaboration with the U. S. Forest Service, the oil has been studied in this laboratory during the past year. Well identified trees were selected in Florida. The trees were regularly chipped throughout one season of eight months. The product from each tree was collected every eight weeks. The oleoresin closely resembles that from Cuban pine (*P. heterophylla*) being quite liquid and containing relatively about the same proportion of crystalline acids. To this low percentage of crystalline matter is to be assigned doubtless, as in the case of *P. heterophylla*, the absence of "scrape" formation on the scarified surface of the tree, a formation so typical of *P. palustris*.

The volatile oil was distilled from the oleoresin by steam in the apparatus described on page 865 above. The oleoresin evidently contains a greater proportion of mucilaginous substances than that from the more common pines, for it was much more difficult to distil. On heating to 140°, the usual temperature of distillation, and introducing steam, the easily molten mass froths badly. This could be avoided only by raising the temperature at the outset to 160°. At this temperature, the viscosity is diminished sufficiently to enable a complete distillation to be carried out without frothing. During the latter part of the summer, however, and during the autumn, the amount of this mucilaginous substance evidently increased, and to such an extent that it became practically impossible to distil off the volatile oil. Partial success was secured by the addition of concentrated sodium hydroxide solution to the distilling flask.

The resin left after distillation is pale yellow, similar to the best grades of commercial resin. Acid number 167.

The volatile oil, freed from water by standing in contact with calcium chloride, was a limpid liquid with a fragrant odor suggesting at once the presence of limonene. The physical constants of the oil follow:

Sp. gr.: 20°, 0.8478.
Sp. rotation: 20°, —105°36′.
Index of refraction: 20°, 1.4734.
Acid number: 0.
Saponification number: 1.54.
Iodine number: 378.
Solubility in ethyl alcohol at 22.5°:

95 per cent. alcohol	1.35 parts required to dissolve 1 part of volatile oil.
90 per cent. alcohol	4.80 parts required to dissolve 1 part of volatile oil.
85 per cent. alcohol	8.10 parts required to dissolve 1 part of volatile oil.
80 per cent. alcohol	16.20 parts required to dissolve 1 part of volatile oil.
70 per cent. alcohol	56.00 parts required to dissolve 1 part of volatile oil.

Comparative evaporation with the volatile oil of *P. palustris*, at room temperature, in shallow watch glasses, 0.2 gram of each used.

Time.	*P. palustris.* Per cent.	*P. serotina.* Per cent.
Loss after ½ hour	35.7	20.30
Loss after 1 hour	62.5	37.30
Loss after 1½ hours	91.7	53.40
Loss after 2 hours	96.0	68.47
Loss after 5 hours	97.8	98.8

On fractionation the following results were obtained:

Temperatures.	Per cent. distillate.	Index of refraction, 20°.	Rotation in 100 mm. tube 20°.
172–175°	27.4	1.4716	—87°53′
175–180°	57.0	1.4724	—92°21′
180–185°	8.4	1.4744	—92°14′
185–+	7.2	1.5045	....

Repeated fractionation at atmospheric pressure showed some polymerization. From a fraction, 175–176°, a large yield of limonene tetrabromide was obtained. Melting-point 103°–104°. The solution of the tetrabromide in chloroform was levo-rotatory, —70.0°.

A study of the oxygen absorbing power of this volatile oil in comparison with that of the ordinary spirits of turpentine obtained from *P. palustris* showed a much larger absorption by the oil of *P. serotina* during the early days of the experiment, but the total absorption after three months' exposure to northern light was practically the same in each.

UNIVERSITY OF NORTH CAROLINA,
CHAPEL HILL, N. C., February 4, 1908.

ON THE OXIDATION OF OLIVE OIL.

BY AUGUSTUS H. GILL.

Received February 14, 1908.

Some years ago it became a question of the determination of the kind of "wool oil" that had been employed in the manufacture of certain "tops." Tops may be defined as wool roving or wool which has been partially spun. In their manufacture the wool is scoured and oiled, usually with an olive oil emulsified with either ammonia or sal soda, then it is carded and spun. As the tops are stored "in the grease," as the expression is, two months may elapse before they are used, so that the oil spread over these fibers has ample opportunity for oxidation.

The oils extracted from the tops had the characteristics shown in the table below:

Top. No.	1.	2.		3.	4.	
Date left mill....	Aug.	Nov.		Nov.	Nov.	
Date tested.....	Jan.	Dec.	Jan.	Jan.	Dec.	Jan.
Iodine No.....	39	53.6	42.1	45.5	54.0	40.5
Saponif. No.....	213	225	221.5	207.5	216.0	221.5

The January samples were different from those tested in December, although from the same lot.

Ballantyne[1] gives the following iodine figures for olive oil which had been "kept in direct sunlight, uncorked and agitated every morning."

Original oil.	1 month.	2 mos.	3 mos.	5 mos.	6 mos.
83.2	82.5	82.3	81.6	79.1	78.2

Sherman and Falk[2] give the following figures:

	Fresh.	Exposed.
Olive oil	83.8	77.4
Lard oil	73.3	66.7
"	69.3	54.6
"	73.3	56.2

From the results obtained from the oils extracted from the tops it would seem that the oil could not have been by any possibility olive oil.

As an aid in settling this question, olive oil was exposed to atmospheric agencies under varying conditions, as follows:

I. Olive oil A was emulsified with ammonia and soda in the usual way, the emulsion sprinkled upon absorbent cotton and allowed to lie in the laboratory for seven weeks, covered with paper to keep off dust. The time (seven weeks) was approximately equal to that which the oil had been upon the top when received. The oil was then extracted from the cotton (sample B).

II. Another portion of olive oil A was emulsified as in I and extracted from the emulsion by ether (sample C). This was to see what effect, if any, the emulsification process had.

III. A portion of olive oil A was oxidized by drawing a current of air through it eight hours per day for seven weeks (sample D).

IV. A fourth portion of the original olive oil was allowed to stand for this same length of time in an open beaker in the laboratory (sample E).

V. Another portion of the original oil was emulsified and sprinkled upon the tops themselves, which had been extracted with naphtha and allowed to remain for five weeks as in Experiment I. The oil was then extracted (sample F).

VI. Lastly a sixth portion was heated for two hours in an open dish to 120° to see the effect of heat (sample G).

TABLE OF THE OXIDATION OF OLIVE OIL UNDER VARIOUS CONDITIONS AS SHOWN BY THE IODINE NUMBER.

A. Original oil.	B. Emulsified oil from cotton.	C. Emulsified oil by itself.	D. Blown oil.	E. Open beaker oil.	F. "Top" oil.	G. Heated oil to 120°.	H. Original oil after standing 7 weeks, closed.
83.2	62.0	84.0	84.0	83.9	78.2	82.0	83.5

[1] *J. Soc. Chem. Ind.*, 10, 29.

[2] THIS JOURNAL, 27, 606.

The iodine number of the oil supposed to have been used on the tops at the mill was 84.3; assuming that the change was the same as in the laboratory, that upon the tops should not have been below 63 or certainly should not have reached 53–54, as both my determinations and that of the mills chemist showed.

The work corroborates that of Ballantyne and shows that except when spread out in a finely divided condition as upon cotton, olive oil changes but little on exposure to the air or heat.

The high saponification numbers, 207–221, indicate that the oil has undergone oxidation and also the entire absence of any unsaponifiable or mineral oil. It would seem from these results that the oil used upon the tops was most likely lard oil; had it not been for the possibility of cholesterol in the wool this could have been shown by a test for cholesterol in the extracted oil.

In conclusion, the writer wishes to express his indebtedness to Mr. H. S. Bailey, by whom the analytical work was performed.

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THE EFFECT OF TEMPERATURE ON THE RESPIRATION OF APPLES.

BY FRED W. MORSE.

Received February 17, 1908.

While engaged in an investigation of the effects of different methods of storage on the chemical composition of apples, it was found impracticable with the methods of analysis in common use to determine the variations produced by comparatively small changes in temperature, or in other words, whether 32° F or 45° F affected the composition of the fruit in a different ratio.

This difficulty was due to the fact of the destruction of some of the apple constituents by respiration, which could be easily deduced from the exhalation of carbon dioxide and water, and the practically constant proportions of water and dry matter which existed in spite of a steady loss of water, and decrease in weight.

It seemed possible that the rate of chemical change might be measured by determining the rate of exhalation of carbon dioxide. Some simple experiments with fruit under bell jars, over mercury, and over water, soon showed that temperature had a very marked effect on the exhalation of the respiratory products.

A respiration apparatus was planned and constructed as follows: The chamber in which the fruit was to be placed was a cylindrical vessel of copper supported by a tripod in an upright position. The bottom of the cylinder was formed like a funnel ending in an outlet tube of brass

to connect with absorption apparatus. The top of the cylinder was closed by a disc of glass, which rested on a narrow shelf soldered to the inner wall of the cylinder. An inlet tube entered the cylinder just beneath the shelf.

The dimensions of the cylinder were, diameter 20 cm., height 25 cm., and conical bottom 5 cm. in depth. The shelf for the glass plate was 2 cm. below the upper edge. The total volume was a little more than 6 liters. The inlet and outlet tubes were 6 mm. in diameter.

The respiration chamber was placed inside a larger galvanized iron tank, which could be filled with ice or water in order to control the temperature. The outlet tube was passed through a tubulure near the bottom of the outer vessel. The inlet tube was passed through a hole in the cover of this vessel, led to a point near its bottom, then coiled around the tripod and, finally, soldered to the inlet orifice near the top of the respiration chamber.

Air, before entering the chamber, would thus be brought to the temperature of the surrounding tank, and the carbon dioxide would fall and accumulate in the funnel-shaped bottom. A slow current of air would maintain a constant temperature within the respiration chamber and the carbon dioxide would be readily removed because of its density.

The air was freed from carbon dioxide before entering the chamber by passing it through a solution of potassium hydroxide. The exhaled carbon dioxide was collected in two absorption tubes connected with the outlet. The first tube contained a 20 per cent. solution of potassium hydroxide and the second tube a standard solution of barium hydroxide. The determinations were made by titrating the alkaline solutions with half-normal hydrochloric acid.

In titrating the potash solution, phenolphthalein was added as an indicator and the acid added until neutral, then methyl orange was added and an exact measurement made of the amount of standard acid now required to neutralize the potassium hydrogen carbonate. The barium solution was titrated with the standard acid and phenolphthalein.

In the majority of experiments the potassium hydroxide absorbed all the carbon dioxide.

The procedure in an experiment was as follows:

About 2 kilograms of sound Baldwin apples were placed in the respiration chamber, and the glass disc was firmly sealed in place with putty. A current of air was drawn through the apparatus by means of an aspirator holding about 16 liters of water. The rate of flow was adjusted so that the air would be renewed three or four times during the experiment, and yet not pass too rapidly to permit complete absorption of the gas by the alkaline solution.

Blank experiments were repeatedly made to include the carbon dioxide,

which might leak in, together with that in the atmosphere of the empty chamber and the amount present in and absorbed by exposing the solutions while filling and emptying the absorption tubes, and titrating. Corrections were then made by deducting results of blank tests from the amounts obtained in experiments with the fruit.

The leakage gave but 2 to 3 mg. of carbon dioxide; but the contamination of the solutions was of considerable consequence, requiring about 2.5 cc. of the half-normal acid to correct it.

The earlier experiments were conducted only during the day, because the aspirator was found unreliable in maintaining a continuous current of air. Therefore, each morning, air was drawn rapidly through the chamber until its atmosphere had been renewed repeatedly, before the absorption tubes were attached for the collection of the exhalations.

Later in the season, a larger aspirator was employed by which a continuous run could be maintained for two days or more at a time. Some of the experiments were made at room temperatures, some with the outer tank filled with ice-water, and some with it filled with closely packed ice. No attempt was made to regulate the temperatures closely, during these trials, but readings of a thermometer in the room or in the outer tank were recorded.

Since the weights of fruit and length of time varied with different experiments, the amounts of carbon dioxide were calculated on a common basis of one kilogram of fruit and one hour of time, and the quantities expressed in milligrams.

The data of the different runs follow, with the results arranged in groups, according to the temperatures. The room temperatures and the ice-water temperatures ranged through several degrees, but all results are included.

CARBON DIOXIDE EXHALED BY 1 KILO OF APPLES PER HOUR.

Room temperature, 18° to 25° C.			Medium temperature, 5° to 10° C.			Low temperature, 0° C.		
	Hrs.	Mgs.		Hrs.	Mgs.		Hrs.	Mgs.
Oct. 16	8½	16.4	Oct. 22	5	8.0	Oct. 29	22	2.3
Oct. 17	5	18.7	Nov. 7	6⅛	7.3	Oct. 30	6⅓	2.6
Nov. 5	6¼	12.6	Dec. 2	5½	8.7	Nov. 8	8	3.8
Nov. 6	6½	12.6	Dec. 3	6½	9.5	Mar. 2–4	46½	2.4
Nov. 12	6¼	18.2	Dec. 4	6⅛	8.8	Mar. 4–6	55¾	2.8
Dec. 9	5⅛	18.0	Dec. 5	7½	7.9	Mar. 9–11	48	2.2
Dec. 10	6	17.9	Dec. 6	5½	9.6			
Dec. 11	6½	23.0	Mar. 16–18	48	5.5			
Dec. 12	6½	26.7						
Feb. 26–28	47	17.9						

It was invariably noticed that a number of hours was required to bring the apples into equilibrium with the surrounding temperature, hence, when changing from room temperature to that of melting ice, the respira-

tion would slowly decrease until it reached the normal rate for the latter environment.

The average rate of exhalation of carbon dioxide was 18 mg. per kilo an hour at room temperatures, 8.1 mg. at medium temperatures, and 2.7 mg. at zero.

A comparison of the results obtained at the different temperatures showed that they were not directly proportional to the variations in temperature, but that there was an acceleration of the rate of respiration as the temperature rose, which corresponded to the law of acceleration of chemical action by rise of temperature.

At room temperature, the amount of carbon dioxide per kilo an hour was about 6 times what it was at 0°. The intermediate temperatures gave an average result which was 3 times that of 0°, and not quite one-half of that at the higher temperatures.

The investigation was now dropped for a time, until an opportunity offered for better control of temperature. Although there was a strong probability that the acceleration of respiration was in accord with the acceleration of chemical action with rise in temperature, there were uncertainties about the actual temperatures involved.

A year elapsed before the investigation was resumed. Particular attention was given to the temperature of the apples between the runs in the respiration apparatus, in order to avoid the lag in temperature change in the apples themselves.

The apples were brought in from a cool storage cellar where the temperature was running between 45° F and 50° F, or 8° to 10° C. It was therefore decided to try the temperature of 10° first, and save the time required to bring the fruit to some other temperature. The temperature of the chamber was maintained by means of ice-water, just enough ice being added from time to time to keep the thermometer in the outer chamber at 10°. The warm room, of course, tended constantly to raise the temperature.

The apparatus was the same used in previous trials. The aspirator was run as rapidly as was consistent with thorough absorption of the carbon dioxide. The same methods of determining carbon dioxide were employed and everything done to make the results comparable with the earlier ones.

The experiments were conducted for several successive days. After the day's run was made, the apples were removed to a large jar and placed in a pail of cold water which sat in the coolest part of the building where the temperature had been noted to remain at about 10° during the night. In the morning of each day, they were replaced in the respiration apparatus and the experiment thus resumed. On one morning the water was found to have fallen to 0° and no run was made on that day.

For the temperature of 0°, the outer tank was kept full of closely packed snow throughout the day. When each day's run was completed the apples were tightly closed in a large jar and buried in a snow-bank out of doors. They were also put out there for about 18 hours before the first run.

Room temperature proved difficult to control. The rooms were hot in the latter part of the day, cool at night and gradually warming during the forenoon. Runs were omitted on days when the morning temperature of the room was below 15°.

The results of the three series of experiments are given below:

Experiment 11. Weight of apples, 1428 grams.
Temperature 10° C.
Mar. 15. 6 hours, carbon dioxide 116.6 mg.

Experiment 12. Weight of apples, 1147 grams.
Temperature 10° C.
Mar. 16. 6 hours, carbon dioxide 93.5 mg.
Mar. 18. 6 hours, carbon dioxide 85.8 mg.

Experiment 13. Weight of apples, 1145 grams.
Temperature 0° C.
Mar. 21. 6 hours, carbon dioxide 38.9 mg.
Mar. 22. 6 hours, carbon dioxide 39.6 mg.
Mar. 23. 6 hours, carbon dioxide 27.5 mg.
Mar. 24 6 hours, carbon dioxide 36.3 mg.

Experiment 14. Weight of apples, 1142 grams.
Temperature 20°.
Mar. 25. 6 hours, carbon dioxide 150.2 mg.
Mar. 28. 6 hours, carbon dioxide 145.2 mg.
Mar. 31. 6 hours, carbon dioxide 154.0 mg.

The results for the different temperatures calculated for an hour and a kilogram of fruit are given below:

Date.	Temperature.	Carbon dioxide. Mg.
Mar. 15	10°	13.6
Mar. 16		13.6
Mar. 18		12.5
	Average,	13.2
Mar. 21	0°	5.7
Mar. 22		5.8
Mar. 23		4.0
Mar. 24		5.3
	Average,	5.2
Mar. 25	20°	21.9
Mar. 28		21.2
Mar. 31		22.5
	Average,	21.9

The acceleration from 0° to 10° is more marked than that from 10° to 20°, but the ratio of 2 to 1 holds practically true and is 4 to 1 for the rise of 20°.

While this work was in progress there was published by Bigelow, Gore and Howard[1] a description of respiration experiments with apples where there were two lots, one at 0° and the other at 15°. These results were given in percentages of the original weights of apples. From their tables it was found that but four dates could be compared, which are given herewith, together with the percentages of carbon dioxide and the ratio between 0° and 15°.

Date.	0°.	15°.	Ratio 0°: 15°.
Jan. 5	0.234 per cent. CO_2	0.794 per cent. CO_2	1:3.3
Jan. 27	0.308	0.899	1:2.9
Mar. 2	0.436	1.122	1:2.5
Mar. 30	0.484	1.375	1:2.8

The average ratio is 1:2.9, which is approximately that of 1:2 for a rise of 10°.

All these results show concordance and prove that apples undergo chemical changes fully twice as fast and in some instances three times as fast with a rise of temperature of 10° between 0° and 20°, or in other words, at summer temperatures apples will undergo respiratory metabolism from 4 to 6 times as rapidly as in modern cold storage. The low temperatures also prove that there must be a limit to the keeping quality even there, since respiration and consequent destruction of cell tissues still goes on.

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OBSERVATIONS ON THE STABILITY OF LECITHIN.

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Numerous investigations published in the last four or five years on the subject of the preparation of the lecithin compounds from eggs or from animal and vegetable tissues have discussed more or less vaguely the stability of these products under the influence of light, heat, and atmospheric oxidation. It seems to be assumed that the lecithins in general suffer very ready decomposition, but in the literature I am unable to find much that is definite as to the extent of their decompositions which take place under the influences referred to. In the course of certain experiments in other directions I found the need of this information and felt obliged to carry out some experiments to supply the desired data.

At the outset it may be said that the conception of the term "lecithin"

[1] *U. S. Dept. Agr., Bur. of Chem., Bull. No.* 94, "Studies on Apples."

is still very vague, in spite of the extended studies of Thudichum,[1] Koch,[2] Erlandsen,[3] Stern and Thierfelder,[4] E. Schulze[5] and colleagues, and others, in addition to the well-known investigations of the older literature, and what may be affirmed of egg lecithin, as we know it to-day, does not necessarily apply in full to an analogous product from the vegetable kingdom or from brains. The extended experiments of Thudichum and Erlandsen have contributed greatly to modify our views as to the brain and muscle extracts of a fatty nature containing nitrogen and phosphorus, while the recent paper of Stern and Thierfelder, referred to, shows in clear light the fact that egg lecithin, generally supposed to be comparatively simple and containing probably two main constituents, must in reality be much more complex; but the relatively small yields secured in the fractionations described in these papers are probably not wholly due to imperfect insolubility, but are much more probably due to partial decomposition of some of the individual substances during treatment. That this is the case is shown further by the rather marked acidity of some of the fractions, which is probably due to separated glycero-phosphoric acid, or other phosphoric acid derivative. The modifying influence of the presence of some of these decomposition products on the reactions of "lecithin" is generally overlooked and will be referred to later.

However, it is not my intention to take up the preparation of various lecithin products at the present time, but rather to present data bearing on the stability of some of the best known representatives of the group, as secured through generally recognized methods. Egg lecithin was taken as the first of these products, as representing the simplest and most readily prepared.

Experiments with Egg Lecithin.

Preparation.—The largest quantity of this used was made from yolks without previous drying. The yolks of 72 eggs were treated in lots of 12 eggs each. In each case 300 cc. of ether were added and shaken with the dozen yellows through several days; this was followed by the addition of 500 cc. of alcohol, after which the mixture was well shaken repeatedly and allowed to settle. The alcohol-ether solution was filtered and evaporated to a pasty condition at a low temperature, and finally by aid of vacuum. The residue was taken up in pure ether, the solution filtered, concentrated and precipitated with pure neutral acetone in excess. This operation of dissolving in ether and precipitating by acetone was repeated three times, the last product being carefully dried in a

[1] "*Die chemische Konstitution des Gehirns des Menschen und der Thiere,*" 1901.

[2] *Z. physiol. Chem.*, 36, 134; 37, 181; and elsewhere.

[3] *Ibid.*, 51, 71.

[4] *Ibid.*, 53, 370.

[5] *Ibid.*, 40, 101, where other literature is cited.

vacuum at a low temperature, but not so as to remove *all* the moisture, as may be done by drying over sulphuric acid through a long period. By drying in the latter way a very hard, horny product is secured, which is not easily worked with later. In several lots prepared in my experiments, the average water content left was 6 per cent. In all, about 90 grams of the final product were secured in the form of a light yellow mass, which, on analysis, showed these results for phosphorus and nitrogen:

	Per cent.
P	3.59
N	1.82

These values calculated to the anhydrous condition give:

	Per cent.
P	3.82
N	1.94

which correspond to an atomic ratio of

P:N::1:1.12,

which suggests a mixture containing some diaminomonophosphatide. With this product the following tests were made, an aqueous emulsion containing in 100 cc. 4.476 grams of the anhydrous substance being employed in most cases.

Effect of Heat.—Two portions of 25 cc. each were evaporated to dryness in a current of carbon dioxide, the temperature being kept at about 60°. The residues found weighed 1.133 and 1.136 grams in place of 1.12 grams, about, as found by long drying over sulphuric acid. This experiment was repeated with three new portions of 25 cc. each. These were evaporated at a temperature of 100° in a vacuum-drying oven, through which a rapid current of carbon dioxide was passed. At the end of two days constant weights were reached as follows:

A.	B.	C.
1.115	1.127	1.122

The dry residues were washed in the small dishes with portions of 25 cc. and then with 10 cc. each of pure dry acetone, the acetone remaining half an hour in contact with the residues. After pouring off the last acetone the dishes were returned to the oven and again dried in carbon dioxide. The new weights found were then:

A.	B.	C.
1.048	1.070	1.063

Nitrogen determinations were made on these residues, which gave the following results:

A. Per cent.	B. Per cent.	C. Per cent.
1.97	1.93	1.95

It is evident that these final residues have about the same composition

as the original, although some loss has occurred in the drying and washing with acetone. This loss is apparently through solubility of the substances as a whole and not through decomposition.

In another experiment 25 cc. of the emulsion were evaporated to dryness in the open air. The product found was very brown and weighed 1.101 grams, that is, less rather than more than the normal. The nitrogen found in it was 0.0214 gram, which corresponds to 1.94 per cent. of the dry weight. In spite of the dark color no important volatile decomposition product had been formed.

Essentially the same result was found by long boiling. Twenty-five cc. of the emulsion were diluted with 50 cc. of water. The mixture was placed in a flask with a stopper furnished with a fine opening and boiled long enough to bring the volume back to 25 cc., which required about an hour and a half. The nitrogen found was 1.94 per cent. again. It is evident that no volatile nitrogen products were formed, and the emulsion remained perfect.

In another experiment 25 cc. of the emulsion were heated in a platinum dish in an autoclave to a temperature of 175°, through two hours. After cooling, the contents of the dish consisted of a clear liquid and a dark fat-like ring on the dish at the surface of the liquid. The total nitrogen in the dish was found to be 0.020 gram, or 1.79 per cent. of the weight of the original dry substance. There was evidently some loss, therefore, of this element.

From these several experiments it is evident that the effect of heat, alone, is not very pronounced, if the conditions for oxidation are absent. It has been noticed in several other cases that even after long heating to 100° in an atmosphere of carbon dioxide, perfect, light-colored emulsions could still be secured, with no change of properties.

Acidity.—The various lecithin preparations which I have examined show a decided acidity to phenolphthalein, and this property in their product is referred to by Stern and Thierfelder.[1] This acidity may be observed directly in the emulsions by titration with 0.1 *N* sodium hydroxide, and more clearly after addition of neutral alcohol. Twenty-five cc. of the above emulsion, containing 1.12 grams of anhydrous lecithin, required directly 1.3 cc. of this weak alkali, and after the addition of alcohol nearly 4 cc. In a second test 1 gram of the lecithin, or 0.94 gram of dry product, was made into an emulsion with 15 cc. of water and 25 cc. of alcohol were added. On titration, I used now 3.6 cc. of the 0.1 normal alkali.

This acidity does not appear to be due to acid liberated on formation of the emulsion with water, as it is also observed on titration of a solution in strong neutral alcohol. A solution made by dissolving 1.157

[1] *Loc. cit.*

grams of lecithin (anhydrous) in neutral alcohol, to which a little neutral ether was added, required 4.2 cc. of the 0.1 normal alkali with phenolphthalein. The acid substance is therefore present in the original lecithin as separated by the process outlined, and the fact that in absence of alcohol a weak acidity is shown, while after addition of the latter a much stronger acidity is developed, is evidence of the presence of two kinds of acid substances. One of them is soluble in water and is indicated in the first part of the titration, while solution in alcohol is necessary to bring out the second substance. It is likely that the glycero-phosphoric acid complex is responsible for the first reaction, while separated fatty acids, on solution in alcohol, bring out the second. Pure glycero-phosphoric acid behaves as a dibasic acid with phenolphthalein and is monobasic with methyl orange, while the acid complex, as separated from lecithin, would doubtless act as monobasic with the first indicator and neutral with the second. The lecithin emulsions I have made are not acid to methyl orange. From the above it appears possible, if not probable, that the acidity observed in the lecithin is due, in part, at least, to small amounts of dissociation or hydrolysis products, rather than to the substance itself. If we may assume that the free acid hydrogen of the phosphoric group is fully combined in the titration in aqueous solution, each cc. of the 0.1 normal alkali used would measure 8.07 mg. of lecithin decomposed, or in the above case, would correspond to about 10 per cent. of the whole. But this assumption cannot be correct, as a part of the phosphoric acid is apparently already combined with calcium. The ash of the lecithin contains this metal, as shown by Thudichum for the brain lecithin, and by Stern and Thierfelder for the egg product. Further light on the question of acidity will be given in some experiments to be referred to below.

Electrical Conductivity.—Since a determination of electrical conductivity seems to furnish very interesting evidence as to the progress of hydrolysis or other change with liberation of acid in the lecithin emulsion, I have made a large number of tests on this and other samples of lecithin from various sources. At best, the conductivity is low, and its range is indicated in the following table. The measurements were made by the usual Kohlrausch telephone method, and always at a temperature of 20°, accurately maintained. The lecithin was made into an emulsion with water of high purity, the conductivity of which may always be neglected for these tests. The emulsion employed contained, like the one referred to above, 4.476 grams of anhydrous lecithin in 100 cc. The variations in the conductivity with the dilution are shown below.

The emulsion once formed, is comparatively stable, as shown by this experiment. Twenty-five cc. of the original were mixed with 75 cc. of water and heated on an actively boiling water-bath two hours, in a flask. After

cooling, the remaining liquid was made up to 100 cc., accurately, and the conductivity found. It was κ_{20} = 0.000300, that is essentially the same as in the second dilution below.

Conc. in 100 cc.	κ_{20}.
4.476	0.000798
2.238	0.000508
1.119	0.000299
0.559	0.000172
0.279	0.000096
0.140	0.000054

To what is this conductivity due? In the usually accepted formula for lecithins there is a free hydrogen in the phosphoric group, but as intimated above, the acid value of this must be low. In the preparation of these lecithins, alcohol, ether and acetone of a high degree of purity were used throughout. These liquids were tested for conductivity and residues from evaporation of 50 cc. of each one, taken up with water, were also tested. In no case was a conductivity found which was at all appreciable. The triple solution in ether and precipitation by acetone insured the freedom from electrolytes originally present. As a corresponding degree of conductivity has been found in many other samples of lecithin from different sources it would seem to be inherent in the molecule, but that this is probably not the case the next experiment will show. Another emulsion of the same strength as the last was made up and examined in the same cell, which contained the usual platinum black-covered electrodes, with capacity, C = 0.306. The conductivity was found to be κ_{20} = 0.000718. Thinking the nature of the electrodes might have some effect, a new test was made in a cell with bright electrodes and C = 0.383. I found now κ_{20} = 0.000715, and the value was not changed after washing the electrodes with ether and alcohol.

Twenty-five cubic centimeters of the last emulsion were measured out and precipitated with 45 cc. of acetone in a small separatory funnel, and the precipitate washed with 10 cc. and finally with 5 cc. more of acetone. The residue was dried in a current of washed carbon dioxide and emulsified with water to again make 25 cc. In the same cell, with the bright electrodes, I found now a resistance over 10 times as great, or κ_{20} = 0.000066. After standing 18 hours, the result was unchanged. The acetone was evaporated and the residue made up to 25 cc. with water. During the evaporation a small amount of insoluble matter separated, which appeared to consist of some of the dissolved lecithin, but which was very light in color, while the lecithin residues proper are usually quite dark. The aqueous solution contained a soluble substance, or substances, since a conductivity, κ_{20} = 0.001576, was found and on titration 0.8 cc. of 0.1 normal sodium hydroxide was required with phenolphthalein.

The last emulsion was treated anew with acetone, when the surprising observation was made that a very large quantity of the latter must be added. About 100 cc. were required to do now what was accomplished with 45 cc. in the first case, and more was needed to complete and to wash the precipitate. The latter was made up to a 25 cc. emulsion with water, as before, and tested for conductivity, giving $\kappa_{20} = 0.000041$. This very considerable decrease may be here due in part to the loss of the portion soluble in the excess of acetone, but the change in the first case, after precipitation, cannot be so explained. Several experiments have shown that the recovered lecithin, after the first acetone precipitation and washing, is about 88 to 90 per cent. of the original weight. The loss after the second precipitation is apparently much greater, while in an attempt to precipitate a third time, nearly the whole of the substance went into solution with the acetone. The emulsions found after precipitation and taking up with water are practically neutral to phenolphthalein.

It is evident from the above that the observed conductivity of the first emulsion is due to something not true lecithin, and that when this is separated precipitation by acetone is very difficult. To test this point, some of the supernatant acetone from a first precipitation was evaporated and the residue taken up with water. A few drops of this solution added to the second emulsion caused it to precipitate with acetone immediately. The same result was secured by adding a few drops of a very dilute glycero-phosphoric acid solution; in this case a sharp result followed at once, which suggests that this acid may be the fraction split off from the original lecithin and is responsible for the observed behavior. In precipitating lecithin from ether solution by acetone, in the process of preparation, glycero-phosphoric acid and other possible decomposition products seem to be carried down and remain with the finished mass, but in precipitating from an aqueous emulsion this is not the case apparently, and in this way a purer final product seems to be secured. On this point, however, futher work is necessary, as experiments carried out show, in some cases, a slightly lower nitrogen and higher phosphorus content in the so-purified lecithin than in the other, which suggests that the acetone, in presence of water, may have a splitting or hydrolyzing action and leave a residue poorer in the fatty acid groups, and relatively richer in the phosphoric acid group. It is possible, also, that a part of the nitrogen may be split off from the latter as the following figures suggest: Two emulsions were made, having 5 and 6 grams to 100 cc. These were precipitated with acetone, and the residues washed and dried in carbon dioxide without loss. On weighing, it was found that 88.9 per cent. of the original anhydrous lecithin was recovered. The two recovered products were made up into emulsions again and portions taken

for phosphorus and nitrogen determinations, with the following results, considering the recovered lecithin as anhydrous:

	A. Per cent.	B. Per cent.
P	4.27	3.98
N	1.65	1.68

It will be recalled that in the original dry material the nitrogen and phosphorus were 1.94 per cent. and 3.82 per cent., respectively. It is evident, therefore, that some splitting has followed, but the nature of the reaction is not clear, especially in view of the facts of lower conductivity and lower acidity in the last emulsions.

Salt Precipitation.—It is stated above that an emulsion which will not precipitate by addition of acetone, or at best imperfectly, may be caused to yield a good precipitate by the addition of a trace of glycero-phosphoric acid. It was found that weak salt solutions have the same action, and this, with the original weak emulsions, as well as those made up after acetone treatment. In this respect experiments have been made with solution of sodium chloride, barium chloride, silver nitrate and aluminum sulphate in various dilutions and with many other salts in certain molecular proportions. The precipitates are markedly colloidal and do not settle quickly. These findings do not seem to agree with the results of Koch[1] for brain lecithin. According to this author, dilute emulsions of brain lecithin yield precipitates with dilute solutions of divalent metals, but not with mono- or trivalent metals. My findings are quite sharp and conclusive, and, as will be shown below, hold for brain lecithin also.

In this connection another interesting observation was made. It was found very difficult to extract the lecithin from aqueous emulsions by means of ether; in fact traces only seem to go into solution, and this has been observed not only for the simple emulsions used in these experiments, but also in some of the commercial lecithin emulsions on the market. The addition of sodium chloride brings about an immediate solution, which is first shown by the color of the upper layer when the emulsion is shaken with ether in a tube, and which can be proven by decanting the ether layer and evaporating. This behavior seems to depend on the power of precipitating colloidal substances, possessed by many electrolytes, and was shown by several other salts as well as by sodium chloride, but not by urea and sugar, which are crystalline but not electrolytes. Further work is in progress on this interesting reaction.

Digestion Experiments.—The behavior of the fat-splitting ferment of the pancreas was first pointed out, apparently, by Bokay,[2] but his experiments were not extensive enough to show the rapidity of the action. I undertook some investigations in this direction but did not carry them

[1] *Z. physiol. Chem.*, 37, 181.

[2] *Ibid.*, 1, 157.

far, as meanwhile the work of Schumoff-Simanowski and Sieber[1] came to my notice. In their extended experiments the rate of digestion by several ferments in addition to that by the steapsin is satisfactorily demonstrated. My method of work was in principle very different and was intended to show the rapidity of acid liberation rather than the amount liberated.

It is shown above that the pure lecithin in the form of emulsion has little or no conducting power, while that mixed with small amounts of decomposition products shows electrical conductivity in rather marked degree. It was further shown that this was not increased by standing or by warming on the water-bath. I found, in preliminary experiments, that the emulsions, after being mixed with pancreas extracts prepared in the laboratory, and incubated at 40° through a number of hours, showed a greatly increased conductivity and increased acidity. But in such cases part of the increased acidity is often due to the acids formed by changes in the ferment mixture itself by enzymes or bacteria, and in testing several laboratory extracts and commercial pancreas preparations in incubated solutions, I have observed this increased acidity and increased conductivity. In working with the lecithin emulsions it was necessary to guard against this source of error as far as possible by the use of toluene or thymol in making up the ferment solutions, and even the emulsions themselves.

In carrying out the tests the following solutions were used: First, an egg lecithin emulsion of approximately 1 per cent. strength in thymolyzed water. This was found to have a conductivity, $10^4\kappa_{20} = 2.66$. At the same time a moderated active pancreas extract in thymolyzed water was made and this had a conductivity, $10^4\kappa_{20} = 5.27$. A mixture of equal volumes of the two liquids gave $10^4\kappa_{20} = 4.03$. This mixture was kept in the thermostat at 40°, and portions were withdrawn for tests from time to time with the following results:

Time.	$10^4\kappa_{20}$.
0 hours	4.03
3 "	4.12
21 "	6.77
45 "	10.16
69 "	12.50
96 "	13.02

In the 96 hours through which the experiment was carried the conductivity of the pancreas alone increased from $10^4\kappa_{20} = 5.27$ to 6.34, or 20.3 per cent., while the increase in the mixture was 223 per cent.

At the same time there was a very marked increase in the total acidity of the mixture determined by titration with 0.1 normal sodium hydroxide after the addition of alcohol. At the beginning 25 cc. of the mixture re-

[1] *Z. physiol. Chem.*, 49, 50.

quired 1.6 cc. of the alkali, while at the end of the experiments over 6 cc. were required. The increased acidity was about 4.5 cc. of 0.1 *N* alkali which measures a marked degree of acid liberation, including, apparently, part of the phosphoric acid. From the results given above for the increased conductivity of the pancreas solution alone, it is probable that a part of the developed acidity must be due to the ferment itself. This is a point which is usually overlooked in fat-splitting experiments, and it appears to have been overlooked in one of the results of Schumoff-Simanowski and Sieber,[1] in which the acid formed is evidently more than could have been liberated, under the conditions of the experiment, from the lecithin molecule.

Additional Experiments with Egg Lecithin.—Many of the tests made above were repeated with egg lecithin obtained by somewhat different processes, but it will not be necessary to go into the details of the results. Some data from two cases only need be referred to.

In the first of them a product was obtained from boiled eggs by extracting with ether only. The eggs were boiled until thoroughly hardened, and then the yellows were separated and ground up with clear quartz sand without any preliminary drying. The mass so obtained was thoroughly extracted in the Soxhlet apparatus. The crude ether extract was concentrated and the residue dried at a low temperature. It was taken up with dry ether and precipitated with acetone in the usual way. The precipitate was washed with acetone and dried in carbon dioxide. A nitrogen determination gave 2.08 per cent. The electrical conductivity of an emulsion made up as before was found to be much lower than with the former product, pointing, possibly, to the presence of smaller amounts of dissociation products. The purified lecithin obtained by treatment of the emulsion with acetone, when made up into a new emulsion, gave, likewise, a very low conductivity.

In the preparation of this last lecithin from hard-boiled eggs, the mass left in the Soxhlet apparatus after ether extraction, was extracted through several days with redistilled alcohol. The alcoholic solution was evaporated at a low temperature, leaving a considerable residue, in fact nearly as large as that from the ether extraction. Most of this residue was found to be soluble in absolute ether, which was somewhat remarkable, in view of the preliminary treatment. On concentration of the ether solution and precipitation with acetone a light mass was secured closely resembling that from the ether extraction. After repeated washings with acetone it was dried and used as in the other case. A determination of nitrogen gave a high result, *viz.*, 2.34 per cent. This would suggest the presence of a considerable amount of diaminophosphatide, and is not at variance with the results of some of the experiments of Stern and

[1] *Loc. cit*

Thierfelder.[1] A phosphorus determination was not made because of lack of material.

An emulsion was made with the portion not used in the nitrogen test, and this had a concentration of 3.1 per cent. It was characterized by a relatively high conductivity, and for equivalent concentrations almost four times as great as for the portion extracted with ether alone. The emulsions in both cases precipitate metallic solutions readily and both have an acid reaction when tested directly. That the two extracts are markedly different is shown not only by the different nitrogen contents but by the great variation in conducting power. It is apparent that the alcohol has brought a larger quantity of decomposition products into solution than was the case with the ether.

Experiments with Brain Lecithin.

It is well known that the product termed lecithin, as obtained from the brain, is usually a mixture of considerable complexity, and that some, at least, of the constituents of this mixture are very unstable compounds. This is well illustrated by a few commercial substances which are now sold under the name "lecithin," and obtained from brain extracts. In beginning some experiments with brain lecithin, I attempted to use a crude product made by a local manufacturing firm, and which was obtainable in quantity. This material dissolved readily in ether, and the solution gave a good precipitate with acetone, but on attempting to redissolve and purify it, it became dark. Even after repeated solution in ether and precipitation by acetone the products secured remained dark and failed to yield a characteristic emulsion with water. The crude extract had been prepared by extraction with the light hydrocarbon sold as "hexane," and in some stage of the work had probably been exposed to a high temperature, which brought about a marked decomposition. The products of decomposition were evidently carried down with the acetone precipitate in the first and following attempts at purification. I mention these facts because they throw light on some of the commercial "lecithin" preparations on the market, which in recent years have been highly advertised as curative agents.

Not being able to utilize the commercial product, I dried down about a kilogram of minced calves' brains in a current of warm air, as recommended by Erlandsen,[2] and extracted with ether thoroughly. This ether extract was concentrated and the solid portion finally dried at a low temperature in a rapid current of carbon dioxide. The pasty mass was taken up with absolute ether, which left a residue amounting to about 60 per cent. of the crude solid extract, and this new ether extract was concen-

[1] *Loc. cit.*

[2] *Z. physiol. Chem.*, 51, 71.

trated to a small bulk. This was precipitated with acetone, which furnished a nearly white mass. The latter was dried and after expelling the acetone completely was redissolved in absolute ether and again precipitated with acetone in a large flask. The greater part of the supernatant liquid was easily removed by pouring and the remainder was drawn out by a current of carbon dioxide passed rapidly through the flask, which meanwhile was immersed in a vessel of warm water. In this way a good yield of a *light yellow* mass was recovered, with which the following experiments were made. On analysis the phosphorus content was found to be 3.76 per cent. and the nitrogen content 2.15 per cent., both calculated on the anhydrous basis. This gives an atomic ratio,

$$P:N::1:1.27.$$

The product is naturally a mixture of different phosphatides, and for the purposes of the present examination is sufficient. The experience of Stern and Thierfelder[1] shows the extreme difficulty of securing products of constant composition, in quantity, from the analogous egg lecithin, as well as the great losses which accompany re-solution and precipitation.

Effect of Heat.—Tests were made here as with the egg product, and the general results were essentially the same. However, this difference was noted: in all the evaporations, whether of the aqueous emulsion or of the ether solution, the brain product remained much lighter in color than was the case with the other. This suggests a greater degree of stability, although from the apparently greater complexity the reverse might be assumed. After evaporating the emulsions to dryness and making up to the original volume with water, no perceptible change in color followed, and no essential change in conductivity. From my various experiments in this direction I must conclude that the lecithin compound, such as is secured in the method of extraction outlined, is much more stable than would be inferred from many statements in the literature. In the process of preparation, that is, while the lecithin is mixed with other substances, it evidently changes readily, but when isolated is apparently much more stable. In view of many observations I have made, I must consider the statement of Bang[2] on this point as too strong.

Acidity.—The brain lecithin shows a greater acidity toward phenolphthalein than was noted with the egg product. As before, this is best observed in the aqueous emulsion. To test the point quantitatively, an emulsion was made containing in 100 cc. 4.52 grams. When directly tested, 25 cc. of this, containing 1.13 grams, required 2.1 cc. of 0.1 normal alkali for neutralization. For a second 25 cc. mixed with an excess of neutral alcohol, 7.4 cc. of the dilute alkali were required. This is a strong degree of acidity.

[1] *Loc. cit.*

[2] "*Ergebnisse der Physiologie,*" VI Jahrgang, p. 162.

A second 50 cc. of this emulsion was precipitated and washed with pure neutral acetone, using 120 cc. in all. This acetone solution was divided into equal portions, one of which was titrated for acid and then used for a phosphorus test, while the second portion was tested for nitrogen. In the titration, 6.5 cc. of 0.1 normal alkali were required, and this for a volume corresponding to 25 cc. of the original emulsion. A good test for phosphoric acid was also secured. The portion reserved for nitrogen was concentrated and decomposed in the usual manner for the Kjeldahl determination. The ammonia obtained was 12.6 mg., corresponding to nitrogen equivalent to 0.92 per cent. of the original lecithin in the volume taken.

The purified lecithin residue left after the acetone treatment was dried in carbon dioxide, then freed from this gas by a current of air with gentle warming, and made up with water to a volume of 50 cc. A portion titrated was found to be *perfectly neutral* with phenolphthalein and alkali, even after addition of alcohol.

Twenty cc. of the new emulsion furnished 0.0106 gram nitrogen, which amounts to 1.17 per cent. of the anhydrous lecithin originally present in the equivalent volume.

Ten cc. of the emulsion gave 0.0105 gram phosphorus, corresponding to 2.34 of the lecithin originally present in the equivalent volume.

It is evident that the treatment of the emulsion with excess of acetone has resulted in precipitating lecithin, apparently, with considerable loss, and also in changing the ratio of the nitrogen to the phosphorus. In the original substance we had 3.76 per cent. P and 2.15 per cent. N, with an atomic ratio of P:N::1:1.27. Here, in the "purified" emulsion, we have 2.34 per cent. of phosphorus and 1.17 per cent. of nitrogen for the same recovered weight, or a ratio of P:N::1:1.17. In other words, there is a relatively greater loss of nitrogen than of phosphorus, as was found to be the case with the egg product, and the acetone treatment may have then the effect suggested for the egg lecithin.

No quantitative determination of the weight lost on treating the brain lecithin emulsion with acetone was made, but superficial observation showed it was much higher than with the egg lecithin, and besides this the supernatant liquid was not perfectly clear as in the other case. We have then a rather marked degree of solubility in the acetone, and this seems to be accompanied by the formation of some decomposition products which are likewise soluble. It must be recalled, however, that the total acidity of the acetone solution is not greater than the original, but, in fact, a little less, which complicates any attempt at explanation of what actually takes place in the treatment.

Electrical Conductivity.—For these tests some of the same emulsion,

with 4.52 grams to 100 cc., was employed, and the observations were made as before at 20°. The following results were obtained:

Conc. in 100 cc.	κ_{20}.
4.52	0.000721
2.26	0.000529
1.13	0.000337
0.565	0.000195
0.283	0.000111

In general, the values found are not greatly different from those for the egg emulsions. It appears in this case also that precipitation with acetone furnishes a product with much lower conductivity, as was shown by precipitating 25 cc. with acetone, in a bottle, pouring off the acetone and washing several times with fresh portions. The residue was dried in an atmosphere of carbon dioxide and after expulsion of the gas was emulsified with water and made up to 25 cc. again. The conductivity was now found to be $\kappa_{20} = 0.000127$, or about one-sixth of what it was originally. The new emulsion was neutral in reaction. The great change must be due to the loss of decomposition product, rather than to the loss of lecithin itself through solubility.

Some of this last emulsion was allowed to stand about two weeks and examined again to detect a possible increase in conductivity by hydrolysis through long contact with water, but no such increase was found, and this again speaks for the comparative stability of the substance.

Precipitation by Salts.—It was found that emulsions of the egg lecithin are readily precipitated by solutions of several salts and in a manner quite distinct from that described by Koch.[1] Similar experiments were made with the brain lecithin emulsions, and with the same general result, which will not be given in detail here, as the observed relations are made the subject of fuller investigations. Since the completion of the experimental part of this paper, an article by Hoeber[2] has come to hand, in which the author shows that carefully purified egg lecithin made up into emulsion yields precipitates with many neutral salts without regard to valence of the metallic ions. This is in full accord with the results of my experiments.

Action of Light.—In various methods of preparation of lecithin given in the recent journal literature, much is said about keeping the product, as far as possible, in the dark. In some of my experiments I have done this, while in others no such precaution was taken. To test the behavior of light, I have made emulsions of both egg and brain lecithin and allowed them to stand in stoppered flasks through periods of two weeks or more in a well-lighted room with south and west exposure, and part of the

[1] *Loc. cit.*

[2] *Beiträge zur. chem. Physiol. und Path.*, 11, 35.

time in direct sunlight. I have not observed in any of the flasks a change of color, change in acidity, change in conductivity, or change in behavior toward weak salt solutions, from which I am forced to conclude that the light effect, if present at all, is very slight.

Summary of Results.

In this work it has been shown that:

1. Emulsions of egg and brain lecithin are comparatively stable with respect to temperature. Increase of temperature, or long-continued heating of the emulsions does not appear to increase the dissociation as measured by acidity or conducting power. The action of light on the emulsions appears to be very slight.

2. Lecithin emulsions have an acid reaction which is marked. On precipitating the emulsions with an excess of pure acetone the residues left, on being again brought into emulsion form with water, are neutral. Precipitation of lecithin from ether solution by means of acetone seems to furnish a product which becomes acid when treated with water. The acetone precipitation from water effects also some decomposition, shown by change in the P:N ratio.

3. The electrical conductivity found in the emulsions suggests the presence of acid or basic groups, but after purification by acetone the conductivity is so much reduced as to indicate that this phenomenon as observed is not due to the lecithin itself, but to decomposition products. It is likely that many of the reactions assumed to be characteristic of lecithin are due to hydrolysis or other products.

4. Emulsions of both brain and egg lecithin are readily precipitated by weak salt solutions. No relation between the precipitating power and the valence of the metallic or acid ions of the salts is apparent. The extraction of lecithin from emulsions is aided by the addition of salts.

My thanks are due to my assistant, Mr. Frank Gephart, who has made the above lecithin preparations.

NORTHWESTERN UNIVERSITY MEDICAL SCHOOL,
CHICAGO, February, 1908.

ON THE BEHAVIOR OF EMULSIONS OF LECITHIN WITH METALLIC SALTS AND CERTAIN NON-ELECTROLYTES.

BY J. H. LONG AND FRANK GEPHART.

Received March 13, 1908.

Although lecithin may be obtained, like many other fats, in a crystalline condition, its behavior is ordinarily colloidal, and when mixed with a large quantity of water its relation, physically at least, to the colloids is very marked.

Among the properties of the colloids which must be regarded as of the

highest interest, the behavior of their solutions or suspensions toward salt solutions has attracted recently much attention. Hofmeister[1] was among the first to call specific attention to the precipitating action of many solutions on certain proteins, and these suggestions were followed up by extended investigations of Pauli,[2] Spiro,[3] Hardy,[4] and others. The work of Pauli was especially valuable in showing the order of the precipitating power followed by the different cathions, and the modifying influences of the anions, while in the later article of Spiro, data are presented to bring these phenomena in comparison with others and so lead to a theory of the processes.

Considering the lecithins as colloids, Koch[5] has attempted to show the relations between valence of cathions and the precipitation of weak emulsions of this substance by solutions of numerous salts. According to this author the behavior of lecithin emulsions is in many respects analogous to that of the true colloids just referred to, but the precipitating power of the salt solutions on the emulsions seems to be confined to certain groups only. Mono- and trivalent metals are said to be without action, while the solutions of the common bivalent metals, Mg, Ca, Sr, Ba, Co, Ni, Fe, Zn, Cd, Cu, etc., are active precipitants. Acid solutions (H ions) were also found to act as precipitants, while a number of anions, investigated in their combinations with metals of the first group, were found to be without specific action. In this paper Koch notes further the behavior of mixtures of salts in the precipitation of lecithin and finds that certain amounts of the mono- and trivalent metals neutralize the precipitating action of the bivalent metals. This is especially interesting in the case of ferric chloride, which was found to prevent precipitation by calcium nitrate.

While experimenting on the extraction of lecithin from certain solutions and emulsions on the market as remedies, or "tissue builders," we made the observation that the ease or completeness of extraction is very much influenced by the character of mineral matters or salts present at the same time. Emulsions in water or glycerol which gave up no lecithin directly to ether or chloroform were found to extract perfectly by a shaking-out process after the addition of various salts. In following up the question it was found that these salts all produced a more or less perfect precipitation in water emulsions, and that this separation by precipitation, or salting out, must evidently precede the actual ether extraction. As some of this experience seems to be the reverse of that

[1] *Archiv. exper. Path. u. Pharm.*, 25, 1; 27, 295; 28, 210.
[2] *Beitr. chem. Phys. u. Path.*, 2, 1; 3, 225; 5, 27; 6, 233.
[3] *Ibid.*, 4, 300.
[4] *Z. physik. Chem.*, 33, 385.
[5] *Z. physiol. Chem.*, 37, 181.

reported by Koch, we were led to give it a fuller study with a larger number of substances. Before the results were completely worked out, however, an interesting paper by Hoeber[1] came to hand in which he reports observations leading to the same conclusions which we had reached, and which fail to confirm the findings of Koch. As our experiments cover a somewhat wider range than those of Hoeber on this particular point we give them in full, although as far as the simple question of the precipitation of lecithin emulsions by monovalent metals is concerned it might not be considered necessary.

In a previous paper by one of us,[2] on certain properties of lecithin, attention was called to the fact that acetone precipitates from *emulsions* of this substance a product which is different from the original and in some respects purer; at any rate it is free from the acid reaction usually found in the lecithin from other processes. In our experiments, given below, we have used both kinds of lecithin, with practically the same results, and have tried emulsions of various strengths from 0.005 *N* to 0.05 *N*. For all the reported tests, however, we have used the weakest emulsion, which contaned 4 grams to the liter, as the molecular (here normal) weight of the egg lecithin employed is about 800. The preparation of this lecithin is described in the last paper referred to. It may be added that essentially the same results were secured with some brain lecithin, described in the same paper. The weakest emulsion used is so dilute that it may be filtered, yielding an opalescent filtrate in which a precipitate is readily visible. In the first series of tests we used in each trial 5 cc. of the 0.005 lecithin and 1 and 5 cc. of the salt solutions in normal strength, where the solubility permitted. With salts of low solubility saturated solutions were employed. In the table below "t" indicates increased turbidity, "p" actual precipitation, while by "op" a slight increase in opalescence is indicated. The action of a few acids is included in the table given below.

The table shows the wide range of salts which possess the power of precipitating the lecithin emulsions, and the most marked difference which may be noted is in the time required to cause actual subsidence of the several precipitates. We have tried to distinguish between opalescence and the appearance of turbidity, but the distinction in many cases is far from sharp. It will be noticed that the action with acetic acid is weak while with boric acid no effect whatever was observed. The precipitates formed by calcium, strontium and barium salts are at the outset heavier, apparently, than those formed by salts of the alkali metals, but after 24 hours the differences disappear and all the precipitates settle out. In most cases these precipitates do not appear to be true

[1] *Beitr. chem. Phys. u. Path.*, 11, 35 (Dec., 1907).

[2] Long, THIS JOURNAL, preceding article.

chemical unions, as the lecithin may be separated by an extraction process with ether, as referred to below, and as is shown also by the following behavior. After subsidence of the precipitates the greater part of the supernatant liquid may be poured off. This liquid carries, of course, the larger part of the added salt. If the same volume of distilled water is then poured over the precipitate and the mixture shaken a new emulsion is formed which, however, is denser than the original emulsion, and, besides, is not stable. A separation soon follows, due apparently to the presence of small amounts of salt not removed in the decantation. On repeating these operations once or twice, and thus removing all the salt, stable emulsions like the original are secured.

TABLE I.—PRECIPITATION OF 0.005 *N* LECITHIN.

	At once.		In 2 hours.		In 24 hours.	
Salts used.	1 cc.	5 cc.	1 cc.	5 cc.	1 cc.	5 cc.
$NaCl$	op	op	t	p	p	p
KCl	op	op	t	p	p	p
NH_4Cl	op	op	t	p	p	p
$NaNO_3$	op	op	t	p	p	p
KNO_3	op	op	t	p	p	p
NH_4NO_3	op	op	op	t	p	p
Na_2SO_4	op	op	p	p	p	p
K_2SO_4	op	op	p	p	p	p
$(NH_4)_2SO_4$	op	op	p	p	p	p
$CaCl_2$	t	t	p	p	p	p
$SrCl_2$	t	t	p	p	p	p
$BaCl_2$	t	t	p	p	p	p
$Ca(NO_3)_2$	t	t	p	p	p	p
$Sr(NO_3)_2$	t	t	p	p	p	p
$Ba(NO_3)_2$	t	t	p	p	p	p
$Fe(NH_4)_2(SO_4)_2$	t	t	p	p	p	p
$FeCl_3$	t	t	p	p	p	p
$Fe'''(NH_4)(SO_4)_2$	t	t	p	p	p	p
Tl_2SO_4	op	op	p	p	p	p
$Pb(NO_3)_2$	op	op	p	p	p	p
$CdCl_2$	op	op	p	p	p	p
$CuSO_4$	t	t	p	p	p	p
HCl	p	p	p	p	p	p
HNO_3	p	p	p	p	p	p
H_2SO_4	p	p	p	p	p	p
$H_2C_4H_4O_6$	p	p	p	p	p	p
$HC_2H_3O_2$	t	t	t	t	p	p
H_3BO_3	o	o	o	o	o	o

The behavior with ether is indicative of the same thing, that is, the physical rather than the chemical nature of the precipitations. To show this a 0.025 *N* emulsion from the same lecithin as before was used, and to it were added certain volumes of ether and salt solutions. After shaking and allowing the mixtures to stand the ether layer which gradually

separated showed always some color, from the lecithin, even with the weakest dilutions of the salts, as shown in the table below for sodium chloride solutions. Essentially the same results have been found for other salts, and need not be repeated. The color of the ether layer measures roughly the amount of lecithin separated, within certain limits, but it is evident that the amount of salt required to secure the maximum color is soon reached in the successive trials. This amount of salt is small. As the ether becomes colored the water layer below clears up perfectly.

TABLE II.—EFFECT OF MIXING EQUAL VOLUMES OF LECITHIN EMULSION SALT SOLUTION AND ETHER.

Strength of salt solution.	Color of ether layer.
0.00500 *N*	very slight color.
0.00625 *N*	slight, but increased.
0.00830 *N*	more distinctly colored.
0.01250 *N*	decidedly yellowish brown.
0.02500 *N*	marked brown color.
0.05000 *N*	" " "
0.07500 *N*	" " "
0.10000 *N*	" " "
0.12500 *N*	" " "

No increase of color seemed to follow after using the 0.025 *N* salt solution, and this amount appears to be sufficient to separate the whole of the lecithin, as was found in some experiments in which larger volumes were taken for the trials. In the above table the amount taken was 5 cc. of each liquid, but with the larger volumes it was possible to recover most of the lecithin in the ether layers. It was found also that the lecithin was separated as such, and not as a salt or combination. This was shown clearly in two experiments in which sodium chloride and barium chloride were employed in relative excess. The supernatant ethereal layers containing the lecithin were removed, evaporated, and the residues ignited. Only a very minute trace of chlorine was found in either case, and no barium in the second case by the sulphate test. These two tests represent typical cases, as the precipitation by the sodium salt is relatively slow, while that by the barium salt is rapid.

The behavior of salts of cadmium and lead in this respect is interesting. Thudichum[1] has shown that these and several other salts give true chemical precipitates with lecithin in alcoholic solution, and it is important to note their action with emulsions. In making the actual tests it was soon recognized that as far as the simple precipitation is concerned, lead and cadmium salts do not differ essentially from the others of the bivalent group, as Koch[2] points out. In making the precipitates in pres-

[1] *Die chemische Konstitution des Gehirns des Menschen und der Thiere.*

[2] *Loc. cit.*

ence of ether, and after a time decanting the layer of this substance which separated, we found that not more than the minutest traces of the heavy metals had gone into solution. These metals, as all the others, remain in the aqueous layer while the lecithin dissolves in the ether. In making a test for lead in the residue from the evaporated ether, nothing more than a faint coloration with hydrogen sulphide was secured at any time, and this might well come from the slight solvent action of the water held by the ether. The results with some other metals were the same, indicating that the lecithin must exist *wholly* in the colloidal form in the water solution, in which condition it does yield a true metallic combination.

A few experiments have been made with some salts in which one or both ions are relatively weak. In this list are included mercuric chloride, cyanide and acetate, aluminum acetate, chromium acetate, and the sulphates of both metals. With the three mercuric salts the precipitation reactions were extremely faint, if at all present, and on adding ether practically no coloration appeared. This behavior is especially plain in the case of mercuric cyanide, from which it may be inferred that the degree of dissociation of the salts may have some bearing on the problem. With the acetates of chromium and aluminum, very weak reactions were observed. These salts were made by double decomposition between the pure sulphates and lead acetate, and held a trace of lead in the water solutions. Solutions obtained by dissolving the washed hydroxides in acetic acid were even more inert with the lecithin, but these solutions were weaker. With the two sulphates good reactions were noticed.

In carrying out the last experiments it was observed that the age of the lecithin emulsions has some influence on the results. Old emulsions appear to be much less reactive than fresh ones, as we noticed in a number of the later tests. With an emulsion which had been prepared several days, no reactions were obtained with the acetates of aluminum and chromium, and rather weak tests with the sulphates. The results reported above were obtained with fresh emulsions in general, and we have carried out no tests to explain this exceptional behavior.

In this connection the action of non-electrolytes is interesting. It was stated above that ether fails to extract lecithin from glycerol emulsions, and in following up this point glycerol, glucose, saccharose, urea and egg albumen were added in molecular proportions to the same kind of emulsion used in the other tests. With the glycerol no increase of turbidity was observed, while with the others it is possible that there was a little increase in the opalescence. According to Pauli, as quoted above, the sugars, urea and other non-electrolytes have no action on the true colloids. With some specimens of urea a slight precipitate may be obtained, but this is due, doubtless, to the traces of sulphates

present in much of the product as obtained from chemical dealers. With pure urea the reaction is extremely weak. On adding ether to the mixtures, and shaking, as before, no color was found in this when it came to the surface on standing. These compounds cannot have, therefore, the same action on the emulsion which was noted with the salts. When, however, to each one of the mixtures a few drops of salt solution were added, and the tubes shaken, an immediate coloration of the ether layer followed as with the regular electrolyte solutions, described above. The extraction with ether is again seen to depend on preliminary salt action, and the presence of the non-electrolytes does not appear to inhibit this. It is possible that some of these substances form loose compounds with the lecithin which are not soluble in the ether, but which are readily decomposed by the addition of salts. A number of such compounds have been described,[1] but in most cases tangible proofs of their existence are lacking. From various physiological reactions the existence of combinations between lecithins and certain toxins has been much better established.

An important combination, however, has apparently been completely overlooked, and that is, the complex formed by the union of lecithin and bile salts. Lecithin in the form of emulsion is dissolved perfectly in an aqueous solution of bile salts, and in considerable proportion. The combination formed seems to be remarkably stable, and not readily decomposed in such a manner as to give up the lecithin to the usual solvents. We are at present engaged in a fuller study of this complex, which is interesting from several standpoints, especially in the separation of lecithin from bile.

Results.—It has been shown in these investigations that weak emulsions of lecithin are precipitated by a large number of solutions of salts and acids and that the completeness of precipitation does not appear to bear any relation to the valence of the cathions concerned. Within each group, the alkali group for example, we have not been able to distinguish any characteristic differences. It seems to be true, however, that the precipitation is in some way related to the degree of dissociation of the various compounds. While, for example, the ordinary acids and tartaric acids are very active, acetic acid is weak and boric acid quite inert. The mercuric salts tested were all weak, and the activity decreased from the chloride through the acetate to the cyanide, which is practically inert.

It has been found also that ether and similar solvents have a very slight extracting power for the pure aqueous emulsions, which in most cases is scarcely appreciable, and that after the addition of salts to the

[1] See convenient literature references in paper by Ivar Bang in *Ergebnisse der Physiologie*, 6, 163.

emulsions the lecithin is immediately taken up by the solvents. This action, which is best shown with ether, is related to the precipitating power of the salts, and it appears necessary to break up the emulsions before extraction is possible. Mercuric cyanide and boric acid do not precipitate the emulsions and after treatment with ether no lecithin is dissolved by the latter.

Certain non-electrolytes tested do not appreciably precipitate the emulsions, and their presence does not aid the solution by ether, but the addition of traces of salt solutions to the mixtures brings about an immediate solution of the lecithin, even when great excesses of the non-electrolytes are used. This behavior has certain practical applications.

Finally, attention is called to the peculiar behavior of bile salts.

NORTHWESTERN UNIVERSITY MEDICAL SCHOOL, CHICAGO.

ON THE OCCURRENCE OF COPPER IN OYSTERS.

BY J. T. WILLARD.

Received March 19, 1908.

Last spring the attention of Dr. S. J. Crumbine, secretary of the Kansas State Board of Health, was called to some cases of illness following the use of fresh oysters in which these were suspected to be the cause. Two samples were sent to the writer for examination. They had a distinctly greenish blue color, and qualitative tests showed the presence of copper. The oysters also possessed a noticeable coppery taste. Quantitative determinations of the amount of copper were made. One of the samples was found to contain 0.0437 per cent. of copper, or 0.302 per cent. calculated on the dry substance; the other contained 0.0324 per cent., or 0.211 per cent. in the dry substance. As copper has been recognized as a constituent of many species of mollusks it seemed desirable to test other samples. Two other samples of fresh oysters and six samples of canned oysters, sold under the name of Cove Oysters, were examined and in every case copper was found to be present. As the oyster season was practically at an end at that time, further investigation was postponed until October, when analyses were made of a considerable number of samples secured chiefly with reference to determination of water content. In all 34 distinct samples were analyzed. The results are shown in the following table.

With the exception of those marked as bulk samples these oysters were placed in glass jars as they were taken from the shells. In most cases the amount of liquor present was too small to determine the copper, but in other cases where the liquor was examined copper was found present, and in no instance was copper absent from the oysters although in sample No. 12,117 the amount was very small. The uniformity of the

TABLE SHOWING COPPER IN OYSTERS.

Serial number.	Place of purchase.	Name.	Per cent. of copper in Liquid.	Meat.	Sample.	Dry sample.
12,094	Manhattan	Bulk, "Booth's"	...	0.0072	0.0072	0.087
12,095	"	" "	0.0056	0.0083	0.0072	0.079
12,096	"	" "	0.0016	0.0084	0.0071	0.079
12,097	"	" "	.....	.....	0.0062	0.059
12,098	Washington, D.C.	Bulk, No. 1	.....	.....	0.0084	0.085
12,099	" "	Bulk, No. 2	.....	.....	0.0022	0.023
12,100	" "	Curryoman	0.0048	0.0056	0.0052	0.055
12,101	" "	Rockaway.	0.0048	0.0060	0.0055	0.043
12,102	" "	York River	0.0024	0.0056	0.0042	0.034
12,103	" "	Hampton Bars	0.0064	0.0056	0.0061	0.058
12,104	" "	Cape Cod	0.0048	0.0068	0.0058	0.040
12,105	" "	Blue Points	0.0016	0.0064	0.0041	0.029
12,106	" "	Coam River	.....	.....	0.0058	0 044
12,107	" "	Blue Points	.....	.....	0.0044	0.034
12,108	" "	Lynnhaven Bay	.....	.....	0.0104	0.064
12,109	" "	Rockaways	.....	.....	0.0080	0.060
12,110	" "	Clarke River	.....	.....	0.0008	0.006
12,111	Philadelphia	Tucker Salts, Barnegat Bay	.....	.....	0.0076	0.052
12,112	"	Rockaway, Partial Salts	.....	.....	0.0032	0.018
12,113	"	Chituque Salts, Jersey Coast	.....	.....	0.0068	0.048
12,114	"	Maurice River Cove, Baltimore Bay	.....	.....	0.0008	0.006
12,115	"	Cedar Rock Salts, Jersey Coast	.....	.....	0.0016	0.012
12,116	"	Maurice River Cove, transplanted	.....	.....	0.0048	0.032
12,117	New York	Cape Cod	.....	.....	0.0032	0.021
12,118	"	Lynnhaven, Va.	.....	.....	0.0008	0.005
12,119	"	Rockaways, Long Island	.....	.....	0.0052	0.047
12,120	"	Blue Points, Long Island	.....	.....	0.0092	0.071
12,121	"	Sea Puits	.....	.....	0.0072	0.051
12,122	Baltimore	Easton Bay, Md.	.....	.....	0.0076	0.087
12,123	"	Lynnhaven	.....	.....	0.0164	0.170
12,124	"	Chester River	.....	.....	0.0084	0.110
12,125	"	Horn Harbor	.....	.....	0.0028	0.025
12,126	"	West River, Md.	.....	.....	0.0048	0.052
12,127	"	Swamp Point	.....	.....	0.0028	0.038

presence of copper warrants the conclusion that that metal is a normal constituent of oysters. The much larger amounts in the first ones examined should perhaps be regarded as abnormal and may have been due to special conditions, the nature of which is unknown. It is not

improbable that, especially with susceptible individuals, those oysters containing the larger quantities of copper might be a cause of illness.

In respect to the mode of analysis, it may be of interest to state that in most cases the oysters were digested with a minimum of sulphuric acid, as in the Kjeldahl method for the determination of nitrogen, the clear solution was diluted and the copper deposited electrolytically. Check tests of the reagents proved them to be free from copper.

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NOTES.

Notes on Mr. Keen's Paper[1] *on the Volumetric Determination of Zinc.*

Mr. Keen disarms criticism by disclaiming any great originality for the method he describes. Unfortunately he has not selected the best of the old methods, and some of the things he advises are likely to cause trouble.

The methods given for preparing the ferrocyanide solution and for the titration are the very excellent ones described by Dr. Low.

The method given for standardizing is complicated and unreliable. A much simpler one is to partly dissolve a single large piece of high-grade spelter in dilute hydrochloric acid, dilute the solution so that it will contain about 5 grams of zinc per liter and determine the zinc by any reliable gravimetric method. I prefer to determine the zinc as pyrophosphate, as the method is simpler than most, and I have found it extremely accurate. If not more than three-quarters of the piece of spelter is dissolved the solution will contain nothing but zinc, and consequently needs no purification. Two or three liters can be made up at once and used as a standard for many months. If extreme accuracy is required, the zinc should be determined in weighed portions of the solution and weighed amounts be used for standardizing.

In the standardizing and actual analysis the volume of the solution, temperature, amount of free acid and of ammonium chloride, the indicator and the method of using it should be kept within very narrow limits or the results will be unreliable. The effect of ammonium chloride on the amount of ferrocyanide necessary is usually neglected but it is quite important.

Sampling Spelter.—The method proposed is very unreliable and likely to cause errors. It has been condemned by the International Committee at the Congress of Applied Chemistry at Rome. The method they recommend is by far the best, *i. e.*, to saw the slabs and use the sawdust for a sample. It is best to saw each slab entirely in two, it must at least be cut to the middle each time. An ordinary band saw, such as is used

[1] THIS JOURNAL, 30, 225.

for wood, answers perfectly; the saw should have rather fine teeth and be run at a high speed. The feed, of course, must be slow.

Analysis.—Common western spelter containing one or two per cent. of lead will not all dissolve in hydrochloric acid, and the residue is likely to contain both zinc and iron. It should be filtered out, dissolved in nitric acid, evaporated with sulphuric, the lead sulphate filtered out and the filtrate added to the main solution.

The methods of separation proposed are nearly all slow and the accuracy of some, at least, is very doubtful. The method[1] recommended by the Committee of this Society on Uniformity of Zinc Analysis is easier, quicker, simpler and far more accurate than the one proposed, and it is applicable to all zinciferous materials.

Aluminum Alloys.—In many cases the presence of aluminum does very seriously affect the ferrocyanide precipitation.

NEW JERSEY ZINC CO.,
71 BROADWAY, NEW YORK.

GEO. C. STONE.

The Detection and Identification of Manganese and Chromium in the Presence of Each Other.—"To the cold, dilute nitric or sulphuric acid solution of the substance or mixture to be tested is added one or two cubic centimeters of a silver nitrate solution of the ordinary concentration, then a relatively large amount (two to five grams) of solid potassium persulphate, and the whole carefully heated until the evolution of oxygen due to the decomposition of the persulphate is practically over. By this means the manganese is converted into permanganic acid and the chromium into chromic acid. The permanganate color shows itself first and is usually best seen during the first few moments of heating. In order to detect the chromium present (the chromate or dichromate color being usually obscured by the permanganate color), the cooled solution is shaken with one-fourth to one-third its volume of ether, hydrogen peroxide added in excess, and the mixture well shaken. This decomposes the permanganate with evolution of oxygen and converts the chromic acid into perchromic acid, which dissolves to a blue color in the excess of ether. Acetic ester may sometimes be used to advantage in place of ordinary ether." The method is delicate, easily performed in an ordinary test-tube, and convenient in having no filtrations or fusions. In a course of Qualitative Analysis it may be tried either upon the original material or upon the proper group precipitate as one wishes. Halides should be absent and in case much manganese is present only small amounts of the substance analyzed should be taken, otherwise the manganese tends to be precipitated as manganese dioxide instead of being converted into permanganate.

W. J. KARSLAKE.
UNIVERSITY OF IOWA, IOWA CITY, IA.

[1] THIS JOURNAL, 28, 262 (1907).

NEW BOOKS.

Organic Chemistry for Advanced Students. By JULIUS B. COHEN, PH.D., B.Sc., Professor of Organic Chemistry in the University of Leeds. New York: Longmans, Green & Co. 1907. pp. viii + 632. Price, $7.00.

The purpose of this book is to supplement the ordinary text-books of organic chemistry by giving more extended surveys of selected topics of special interest. This is, of course, not a new or unoccupied field, for in this country we have Lachman's "Spirit of Organic Chemistry," and in Germany Ahrens's "Vorträge." The new book covers much more ground than the former, but is not so comprehensive in scope as the latter. It is a publication of the subject-matter of lectures which the author has been delivering to his senior students at the University of Leeds, and its field will appear from a glance at the Table of Contents. The chapters are as follows: Historical Introduction, Isomerism and Stereoisomerism, Stereochemistry of Unsaturated and Cyclic Compounds, Stereochemistry of Nitrogen, Isomeric Change, Steric Hindrance, Condensation, Carbohydrates, Fermentation and Enzyme Action, Purine Group, Proteins, Benzene Theory, Terpenes and Camphors, and Alkaloids. A select bibliography at the close of each chapter lists the more important works on the subject, in addition to which there are full references throughout the text.

The material has been chosen with care and discrimination and is presented clearly and concisely. The publishers' work is well done, type and paper being very satisfactory.

The book is a very useful contribution to the literature of the subject, and should be warmly welcomed by all advanced students and teachers of organic chemistry, for it gives in compact form a conspectus of recent progress along lines of particular interest. Thus, the chemist who has had but little time to keep up with recent investigations in such matters as the stereochemistry of the sugars, the synthesis of terpenes, of alkaloids, of polypeptides, enzyme action, tautomerism, and the like, will find here the desired information.

The reviewer most heartily commends the work to the attention of all interested in organic chemistry. MARSTON TAYLOR BOGERT.

Kurzes Lehrbuch der Organischen Chemie. Von WILLIAM A. NOYES, Professor der Chemie an der Universität Illinois. Mit Genehmigung des Verfassers ins Deutsche Uebertragen von WALTER OSTWALD, und mit einer Vorrede von PROFESSOR WILHELM OSTWALD. Leipzig: Akademische Verlagsgesellschaft, m. b. H 1907. 8°, xxiv + 722. Price, bound, 10.80 Marks.

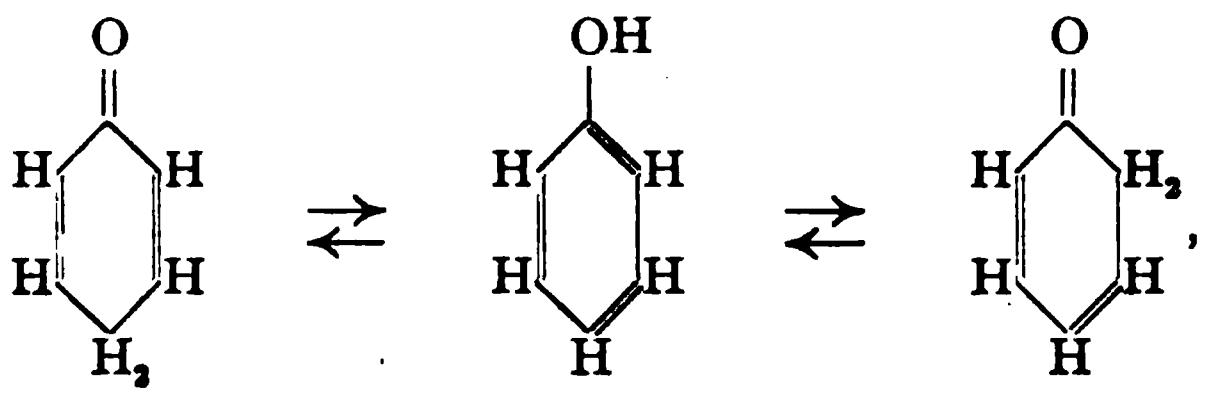
"The justification for adding another volume to the long list of German text-books on organic chemistry, and *that* a translation, must be found in the independent treatment and originality, with which the author conceived and carried out his work. In view of the enormous mass of facts of organic chemistry, it is of decisive importance for every

beginner that he should master as soon and as thoroughly as possible the fundamental points of view connecting these facts systematically. By the original arrangement of its material, the mass of facts has been treated systematically in so logical a way, that the student of this small volume will be able to continue his studies without any fear of losing his way in the thickets of organic chemistry. The author has also solved the difficult problem of suggesting to the student the more advanced fields to be conquered without discouraging him from attempting them. This result has been attained by the great clearness of the style of presenting the subject....."

This free translation of a part of Professor Ostwald's introductory statement to the translation of Noyes's "Organic Chemistry" explains sufficiently the signal honor that this book has received of being rendered into German with the approval of the master mind, in Germany, of the science of the teaching of chemistry.

The writer of this review would recall the fact that the most conspicuous feature in the presentation of material in Noyes's book lies in the fact that the aromatic series of compounds is treated systematically with the aliphatic series. In the first descriptive chapters, all the different classes of hydrocarbons, including benzene and related compounds, are first considered. This arrangement makes it possible to present logically and without unnecessary duplication the reactions of closely related groups of compounds of the aliphatic and the aromatic series, such as the alcohols and the phenols, the amines and the anilines, and so forth. It also makes it possible to discuss at an early stage some of the numerous reactions leading from compounds of one series to those of the other series.

The more critical study of the compounds of the two series is obliterating more and more the lines of any fundamental differences between the two and is recognizing, instead, differentiation in reactivity of groups of compounds of analogous structure common to both series; for instance, it may be recalled that acetacetic ester unquestionably shows the behavior of a phenol, both in its tendency to form salts and in the reactivity of its methine group (:CH—, in the enol form) towards halogens, nitrous acid, diazobenzene, etc. A striking similarity in constitution is obvious if we accept Kekulé's structure for benzene. *Vice versa*, this parallel suggests that even monophenols form tautomeric compounds,



the latter derivatives of a dihydrobenzene, which would account in the simplest way for the comparative ease with which phenol rings are oxidized and opened. It is well-known that the analogy in the behavior of 1,3-dihydroxy- and 1,3,5-trihydroxybenzenes and that of 1,3-dicarbonyl derivatives is even more striking.

The puzzling and central fact that benzene and its derivatives appear to be more stable in the unsaturated condition (Kekulé's formula) and react in most cases as saturated compounds (in the ring) is also not without parallel in the aliphatic series; for instance, the organic acids certainly resist reduction in the unsaturated carbonyl group almost as vigorously as do certain benzene compounds; even when their carbonyl group absorbs certain reagents, yielding temporarily ortho derivatives, there is a rapid reversion to the more stable unsaturated carbonyl group—(in the acid esters, amides, etc.). At the same time this same unsaturated carbonyl group has an unmistakable effect on the activity of the hydrogen of the immediately neighboring groups, *e. g.*, such groups as CH and OH—much as the activity of the hydrogen atoms adjacent to the unsaturated groups of the benzene nucleus is enhanced, and when we have two such neighboring unsaturated groups in aliphatic compounds, *e. g.*, in the 1,3-dicarbonyl series, the analogy is even more marked. Again, we have all degrees of gradation in such relations—the carbonyl group in aldehydes is readily reduced by hydrogen, but towards very many other reagents shows again the same tendency to reversion to the unsaturated condition as a stable form. Benzene derivatives are likewise not all equally resistant to reduction and saturation, as shown by Baeyer, Bamberger and others for the phthalic acids, the naphthalenes and similar compounds. Stability in the so-called unsaturated condition may therefore well be simply a question of peculiarities of structure and energy content, common to all fields of chemistry. It may not be amiss to recall parallel cases of the resistance to saturation of unsaturated compounds in inorganic chemistry, as shown by the phosphines and arsines at ordinary temperatures, and by ammonia above 400°.

The arrangement used by Noyes, treating the aromatic compounds with the aliphatic ones, appears to the writer therefore logical, both pedagogically and scientifically; exhaustive studies of the relation between the two series and especially of the question of stability and reactivity of unsaturated molecules, as made in the investigations of Baeyer, Nef and Thiele, may solve that perplexing problem of the structure of benzene in the simplest of all ways, by demonstrating that there is no real benzene problem, but a broader, greater problem of equilibrium conditions of unsaturated valences.

J. STIEGLITZ.

Exercises in Elementary Quantitative Analysis for Students of Agriculture. By AZARIAH THOMAS LINCOLN, PH.D., and JAMES HENRI WALTON, JR.,

PH.D. New York: The Macmillan Co. 1907. 8vo. pp. xv + 218. Price, $1.50 net.

The work includes introductory exercises in gravimetric analysis, acidimetry and alkalimetry, permanganate and dichromate titrations, iodimetry, stoichiometry, and a section on agricultural analysis covering the examination of milk, butter, cereals and feeding materials, fertilizers and soils.

The book is well written and contains a number of good illustrations. It will be welcomed by those beginners in agricultural analysis who have been obliged to use the methods of the Association of Official Agricultural Chemists in bulletin form in lieu of a text-book. The procedures are clearly and explicitly described and the explanatory notes are generally good. The numerical data selected to illustrate normal composition could in some cases be improved, but the only figures likely to be seriously misleading are those for starch in grain products on page 121.

The failure of the authors to make use of the conceptions of ionization, mass action and solubility product in the discussion of inorganic reactions and the entire omission of electrolytic methods are unfortunate in a text-book which is likely to represent the sole training in quantitative analysis of many of the students who use it. These, however, are omissions which may be supplied by the teacher and which the authors will probably correct in a subsequent edition.

The book will fill a real need in the case of the agricultural student for whom it is especially intended and will be found useful and suggestive to many others. It is commendably free from typographical errors and its general make-up is excellent. H. C. SHERMAN.

Testing Milk and Its Products. By FARRINGTON and WALL. Madison, Wis.: Mendota Book Co. 1908. pp. 292. Price, $1.00.

The authors have revised their useful book. The present constitutes the eighteenth edition, the first edition having been issued over ten years ago. Considerable matter has been added, which includes new methods that have come into recent use. L. L. V. S.

The Chemistry of Commerce. By ROBERT KENNEDY DUNCAN. Harper Brothers. Price, $1.50.

It is perhaps questionable whether "Chemistry of Commerce" should be reviewed in a scientific journal like that of the Chemical Society, inasmuch as the book can only be regarded as a report on certain spectacular topics, some of which barely lie within the broad domains of chemistry.

At the present time, anything which tends to stimulate industrial and applied chemistry in the United States, will be hailed with delight by every chemist of the land. That "Chemistry of Commerce" is intended to do this, is evident from the author's preface and introduction. Whether he has succeeded in stimulating the masses in this highly tech-

nical branch of the science is a question which might best be left to the layman himself. To the chemist, however, who is familiar with the industries of Germany, the value of the book as a stimulus to industrial chemistry lies little above the zero mark. Germany leads the world in industrial chemistry, not because of any attempt to popularize science by means of educating the masses in these extremely technical branches, but because the nation has pursued a diametrically opposite policy. The highly trained few instead of the superficially trained many is the secret of Germany's industrial success.

The book is made up of twelve chapters, some of which have already appeared as magazine articles or "researches," as the publishers choose to call them. The whole is cemented together by both a preface and an introduction with numerous little prefaces thrown in, in order to bring about catalytic action in the mind of the reader.

The author was sent abroad for one year to "write up" the industries of Europe. Evidently the time was too short, for some of the great industries have been left out, or perhaps crowded out by the more pyrotechnical ones like the New Microbe Inoculation. That "laymen subsist on a pabulum of illogical and, for the most part, sensational misinformation," is a stinging blow to scores of popular writers who are moulding public thought and who never appear under the yellow flag. If some one of these writers should consider it worth while, he might, using "illogical" and "sensational," the same standards used by the author, find in "Chemistry of Commerce" hues differing only by a very few wave lengths from the sodium spectrum.

The chapter on alcohol is interesting and reminds one of some of the popular newspaper articles which have appeared from time to time since the new Food and Drug Act. The Ethyl and Maude pun, however, seems a little out of place in any book or article which lays any claims to the science.

Some of the other chapters as, for instance, Catalysis, Fixation of Nitrogen, The Rare Earths, Modern Chemistry and Glass-Making, and Cellulose are too familiar to the reader to need more than mention. Lime nitrogen would probably have had a little more significant meaning to the layman than Kalkstickstoff.

The last chapter on Industrial Fellowship is unique. The scheme is not entirely new. It does, however, seem a little out of place.

In conclusion, let it be hoped that the author may not be disappointed in his method of bringing about a great industrial awakening by his appeal to the public. GEORGE B. FRANKFORTER.

Modern Pigments and their Vehicles. By FRED MAIRE. New York: J. Wiley & Sons. pp. 265. Price, $2.00.

This book is evidently written by a man who has had a great deal of

experience, and contains some very valuable hints, and some excellent descriptions of the composition of pigments. In its chemistry it is a trifle weak. Its style of composition is colloquial, and a publishing house like J. Wiley & Sons should employ a scientific censor whose duty it is to edit a book thoroughly. For instance, the statement that the formula for white lead is $2PbCO_2$ should not be published, but probably this is a printer's mistake. The statement that red lead is a bi-oxide, and orange mineral a ter-oxide is also incorrect.

Under the History and Chemistry of Red Lead, the author states that red lead is the best priming paint for steel and other metals, and that engineers and architects are unanimous in recommending it, and that it is becoming more important every year now that so much structural iron and steel are being used in the construction of buildings in all our large cities. This is only one example of some of the haphazard statements made in the book, because the direct opposite is the case. The Singer Tower, The City Investing Building, the Metropolitan Life Tower and the new Pennsylvania Terminal are four of the largest buildings with steel construction that have ever been built, and not one of them has had red lead applied as a priming or finishing coat, and I do not know of a sky scraper of any importance excepting the Times Building, on which red lead has been used. The author quotes the Norfolk Navy Yard, but inasmuch as the Navy Department in the United States is not progressive, and all their painting is done *in situ*, which is totally different from the shop and field coating of building construction, we cannot attach much importance to naval usage. This would tend to indicate that engineers and architects are anything but unanimous in recommending red lead as a priming coat, and many of the railroads in the United States who do use red lead use a special kind of ready-prepared or ready-mixed red lead which contains a large percentage of reinforcing pigment like silica.

On the other hand, Mr. Maire's book contains some excellent general information for the painter. He has, however, omitted any reference to wood turpentine and China Wood Oil and speaks of naphtha and benzine as materials having a horrible smell.

The chapter on the mixing of tints is excellent, and the general description of the dry colors is very good. The table of synonyms is perhaps the best table of its kind ever published. MAXIMILIAN TOCH.

Technologie der Fette und Oele, Bd. II, Gewinnung der Fette und Oele, Spezieller Teil. By GUSTAV HEFTER, with the collaboration of G. LUTZ, O. HELLER, FELIX KASSLER, and others. Berlin: Julius Springer. 1908. pp. x+974, with 19 plates. Price, 28 Marks.

The first volume of this valuable work appeared in 1907; Volumes III and IV are promised during 1908. Hefter is director of the Aktien-

gesellschaft zur Fabrikation Vegetablischer Oele in Triest. We have a considerable list of books on industrial and technological subjects by college and university professors, by commercial analysts and consulting chemists, but all too few from the pens of those who have attained high rank in the industries of which they write. It is then, with real delight, that we welcome this work on the technology of fats, written by industrial men.

The subject-matter of the present volume is arranged in six general divisions; *viz.*, The Vegetable Oils, The Vegetable Fats, The Animal Oils, The Animal Fats, The Vegetable Waxes, and The Animal Waxes. Under the head of each individual fat, oil, or wax is detailed its history, source, raw material, production, properties, trade relations and economic significance. Methods of analysis are not given, inasmuch as these are to be found well presented and in great detail in such authoritative works as those of Lewkowitsch and Benedikt-Ulzer. In this way the written page keeps faith with the title (a virtue none too common in technological works and worthy of commendation) and the work remains a technology throughout.

The authors have gathered together from a great number of sources and by no means from chemical and technological sources alone, an immense amount of valuable data bearing on the main subject and in point of accuracy few works can boast a superiority to this one. A well-seasoned acquaintance is shown with the special and general literature of the subject and with the patents and processes of various countries. It is pleasing to find the historical side of the subject so capably handled, and at the same time it is a source of satisfaction that the latest mechanical devices and arrangements used in the fat industries are so accurately and fully described and illustrated. Obsolete methods and apparatus, if mentioned at all, are given but the briefest consideration in those portions of the volume treating of modern industrial practice.

Of considerable interest and usefulness are the lists of synonymous terms in various languages as applied to the various oils and fats and the raw material from which they are derived, in the headings of the subdivisions and also in the body of the descriptive text.

The book is a mine of information for the chemist and technologist and it can be heartily recommended to anybody interested in the oils and fats industries.

The paper, typography, general and marginal indexing and the general make-up of the volume are of the usual excellence which characterizes Springer's productions. W. D. RICHARDSON.

Traité Complet D'Analyse Chimique Appliquée Aux Essais Industriels. PAR J. POST, B. NEUMANN. DEUXIÈME ÉDITION FRANÇAISE ENTIÈREMENT REFONDUE, TRADUITE D'APRÈS LE TROISIÈME ÉDITION ALLEMANDE ET AUGMENTÉE DE

NOMBREUSES ADDITIONS. PAR L. GAUTIER. Tome Second-Premier Fasc. Chaux-Mortiers et Ciments-Platre-Produits Céramiques-Verre et Glaçurtes. Avec 99 figures dans le texte. Paris, Librairie Scientifique A. Hermann, 6 Rue de la Sorbonne. 1908.

It is unnecessary for the reviewer to comment at length on this translation from the German of the well known and generally excellent work of Post and Neumann, but it is regrettable that in revising, the translator has not substituted other analytical methods for certain of those described, or at least added to them. For instance, on p. 94, for titanium only the old method of separation by boiling in a nearly neutral solution is mentioned, and no reference is made to the Lawrence Smith method for alkalies. The typography and general appearance of the work are all that could be desired. W. F. HILLEBRAND.

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PAPERS ON SMELTER SMOKE.

[SECOND PAPER.]

ARSENIC IN VEGETATION EXPOSED TO SMELTER SMOKE.[1]

BY R. E. SWAIN AND W. D. HARKINS.

Received January 28, 1908.

In a previous paper[2] there were presented the results of a study of the smoke emanating from a copper smelter now in operation near Anaconda, Montana. It was estimated that at the time the examination was made this plant was discharging daily from its main chimney an average of 59,270 pounds (26,880 kilograms) of arsenic trioxide, along with notable quantities of copper, antimony, lead, zinc, and other substances. The smelter is situated at the base of a ridge which descends steeply from Mt. Haggin, a perennially snow-capped peak rising near the main crest of the Rocky Mountains. On one side of this ridge is the valley of Warm Springs Creek in which the city of Anaconda is situated, and on the other side is Mill Valley, each typical of a number of narrow valleys and ravines leading down from the main range into a broad basin thirty-five miles long and four to six miles wide, the Deer Lodge Valley. The present paper will deal with the distribution of certain of the more notable constituents of the smoke, particularly arsenic, over the district in the vicinity of the smelter. This is a region of variable winds which often blow with great velocity, so the section affected by the solid or gaseous components of the smoke is not confined to a narrow tract nor to any closely circumscribed area. There are prevailing wind directions for each season of the year, but these are not so constant as to restrict the action in any considerable

[1] The work on this paper was begun in 1902 by W. D. Harkins, and was presented in abstract at the New York meeting of the American Chemical Society, December, 1906.

[2] THIS JOURNAL, 29, 970.

degree. Pouring out of the stack a thousand feet above the valley floor, the smoke stream can be traced as far as the eye can reach in that normally clear atmosphere, trailing down the valley for thirty miles toward Garrison, or often eastward in the direction of Butte, or sweeping over into Mill Valley and filling the narrow ravines which lead down from the Continental Divide, fourteen miles to the south. In spite of the height at which it is discharged the smoke may be seen very frequently to strike the valley within less than a mile from the base of the stack, while on quiet days it may rise to a considerable height and hang as a haze over the valley.

The basis of the work herein described has been the vegetation of the Deer Lodge Valley and adjacent territory, and especially the hay and wild grasses, for the primary incentive to the investigation, part of which preceded the examination of the smoke itself, was the claim on the part of the farmers residing in the vicinity of the smelter that they were suffering abnormal losses of live-stock, which they attributed to smelter fumes. The first appearance of the peculiar symptoms of disease in the stock were noticed only a few months after the smelter began to operate; the quick recovery of the milder cases upon removing them to distant pastures, and the recurrence of the disorder on their return; and the fact that the greatest disturbance was observed in those sections over which the smoke drifted most frequently, suggested that the trouble was a local one and in some way connected with the smelter.

In all cases the samples analyzed were collected by one of us or by both of us together, either in stoppered bottles or in heavy glazed jute sampling bags. With very few exceptions the results obtained are from air-dried samples, this being deemed a more reasonable and practical basis to which to refer the analyses than the more complete drying at 100°.

From each of these samples a weighed quantity (30–200 grams) was taken for analysis, placed in a large casserole covered with a watch glass and concentrated nitric acid allowed to stream over it from a pipette. Destruction of the tissue begins at once without the application of heat, and in the case of samples with many leaves which present extensive surfaces for action, the mass may ignite[1] and burn, if not carefully watched during the first stage of the decomposition. Excessive action must be checked promptly by floating the vessel in cold water or, if that is insufficient, by diluting the acid with water. By stirring it occasionally with a glass rod the sample is soon reduced to a thick, yellow, semi-liquid mass after which heat may be applied to the casserole until the most of the acid is expelled. Five to 8 cc. of concentrated sulphuric acid are then added, drop by drop. A rapid decomposition of nitro-compounds fol-

[1] If a large amount of acid is added there is no danger of ignition even if concentrated nitric acid is used.

lows and thereafter the mass is reduced to a charred and crisp condition by heating in an air bath to a temperature not exceeding 180°.[1] If the destruction of the tissue is not perfect enough after the addition of the sulphuric acid, successive small portions of nitric acid may be added during the subsequent heating, taking the precaution to cool the casserole to 100° or less before each addition. This method, which is essentially an application to plant tissue of the Chittenden-Donaldson method for the destruction of animal tissue, yields a final residue capable of easy extraction with acidified water. The extract thus obtained was filtered into a graduated flask and an aliquot part taken for analysis.

In all but a few cases the arsenic was estimated by applying the Marsh-Berzelius method and weighing the mirrors which resulted. In no case in which results are given was an estimate based upon comparative mirrors.

Copper was determined by evaporating another portion of the solution to dryness in a porcelain dish, igniting to destroy all organic matter, and after dissolving the residue in dilute nitric acid, precipitating the copper electrolytically. The following table gives the results of the analysis of vegetable tissue collected in the Anaconda region:

TABLE I.—ARSENIC AND COPPER IN GRASS AND HAY.

Number.	Sample.	Month.	Distance and direction.	Parts per million.[2]	
				As_2O_3.	Copper.
		1902			
1	G[3]	Nov.	0.25 E	1551	1800
2	G	Nov.	3.0 W	166	871
3	G	Nov.	4.0 W	88	708
4	H	Nov.	1.5 S	283	...
5	H	Nov.	3.0 W	36	216
		1903			
6	G	Oct.	4.0 E	10	128
6*a*	G	Oct.	2.0 S	11	...
6*b*	G	Oct.	4.0 SE	13	...
7	H	Oct.	5.0 SE	13	...
8	G	Nov.	15.0 NNE	52	164
9	M	Nov.	15.0 NNE	405	237
		1905			
10	G	Jan.	3.0 N	122	...
11	G	Jan.	5.0 E	100	563
12	G	Jan.	5.0 ESE	90	
13	G	Jan.	2.0 SSE	79	176

[1] Another method used by one of the writers will be described in a subsequent paper.

[2] Parts per million are equivalent to ten-thousandths of 1 per cent., and multiplied by 0.7 give the number of grains in 100 pounds of substance.

[3] H denotes a sample of hay taken from the stack; G, a sample of grass cut from the field; L, leaves of trees; B, bark of trees; C, leaves of the cedar; and V, leaves of the lily-of-the-valley.

TABLE I (*Continued*).

Number.	Sample.	Month.	Distance and direction.		Parts per million. As_2O_3.	Copper.
14	G	Jan.	4.0	SE	50	80
15	H	Jan.	2.0	SSE	23	11
16	G	Jan.	2.5	SW	87	81
17	G	Jan.	4.0	ESE	68	150
18	H	Jan.	3.0	SE	8	51
19	G	Jan.	6.0	NE	170	226
20	H	Jan.	4.2	NE	85	
21	H	Jan.	3.0	NE	96	326
22	G	Feb.	3.0	N	77	112
23	G	Feb.	2.0	N	220	119
24	G	Feb.	4.5	N	217	407
25	H	Feb.	4.0	SE	22	...
26	H	Feb.	4.0	SE	21	...
27	H	Feb.	5.0	ESE	50	46
28	G	Feb.	6.0	N	30	112
29	G	Feb.	5.0	N	263	470
30	G	May	35.0	N	35	...
31	H	June	4.5	N	89	161
32	G	June	6.0	N	67	...
33	H	June	12.0	NNE	35	190
34	H	June	2.0	W	15	...
35	H	June	14.0	NNE	34	221
36	G	Sept.	6.0	N	61	...
37	L	Sept.	0.5	W	427	...
		1906				
38	G	Feb.	5.0	SE	140	
39	G	Feb.	5.5	N	180	
40	H	June	3.0	W	14	
41	G	June	4.0	W	99	
42	H	June	3.0	E	107	
43	H	June	4.0	E	18	
44	G	July	4.2	N	12	
45	G	July	8.0	NNE	111	
46	G	July	5.0	W	38	
47	G	July	3.0	SE	21	
48	G	July	1.5	SW	157	
49	G	July	2.0	S	10	
50	G	July	2.0	SW	359	
51	G	July	1.5	SW	460	
52	G	July	1.7	SW	293	
53	V	July	1.7	SW	583	
54	B	July	1.5	SW	350	
55	B	July	1.7	SW	376	
56	G	July	6.0	N	18	
57	C	July	2.0	SW	508	
58	G	July	0.7	SW	431	
59	H	Aug.	6.0	E	31	
60	B	Aug.	1.5	SW	300	
61	L	Aug.	1.7	SW	683	

TABLE I (*Continued*).

Number.	Sample.	Month.	Distance and direction.		Parts per million. As_2O_3.
62	G	Aug.	1.7	SW	482
63	G	Sept.	2.5	NW	81
64	G	Sept.	2.5	SW	100
65	G	Sept.	6.0	N	33
66	G	Sept.	4.2	N	34
67	G	Sept.	1.0	N	101
68	G	Sept.	1.0	E	236
69	G	Oct.	10.0	SW	64
70	G	Oct.	13.0	SW	38
71	G	Oct.	35.0	N	29
72	G	Oct.	34.0	N	21
73	G	Nov.	4.2	NNE	121
74	G	Nov.	6.0	NNE	73
75	G	Nov.	1.5	E	705
		1907			
76	G	Jan.	1.0	NE	265
77	G	Jan.	2.0	SE	97
78	G	Jan.	3.0	SSE	51
79	G	Jan.	4.0	SE	86
80	G	Jan.	4.0	SE	76
81	G	Jan.	6.0	SSE	47
82	G	Jan.	6.5	SE	98
83	G	Jan.	8.0	SE	79
84	G	Jan.	100.0	NW	00
85	G	Jan.	75.0	W	00
86	G	Oct.	100.0	NW	00

A few of the above samples were analyzed by each of us, using the same balance sensitive to 0.005 mg., but otherwise independently, and the mean of the results obtained taken for the table above. The complete data for each joint determination are given as follows:

TABLE II.

No.	Sample.	Per cent. As_2O_3. H.	S.	Difference. Per cent.
11	Grass	0.0103	0.0097	0.0006
16	Grass	0.0089	0.0085	0.0004
19	Grass	0.0169	0.0170	0.0001
20–31	Hay	0.0089	0.0085	0.0004
22	Grass	0.0079	0.0075	0.0004
23	Grass	0.0219	0.0220	0.0001
29	Grass	0.0264	0.0261	0.0003
33–35	Hay	0.0034	0.0035	0.0001

In all but two cases of those cited above the results given are merely duplicate determinations made on a single sample, but samples 20 and 31 and samples 33 and 35 were instances where each of us took a sample from a stack independently of the other and conducted a separate determination.

The first samples taken from this district were collected in November, 1902, but the record of all except nine of the results of the analyses made on this material and that of the following year was accidentally destroyed. The smelter started early in 1902 and continued without interruption throughout that year, so the results for grass represent a deposition of arsenic extending over a period of six months, while the hay, cut in July, was exposed less than three months. Samples 2 and 5 were taken from the same farm, but one was left exposed in the field during the whole period while the other was removed and stacked as hay. The difference here shown in the two values, 166 and 36, respectively, is fairly representative of a condition which will be found to prevail with notable uniformity throughout the analyses. An interesting exception is found in the data for 1903, where samples 6 and 7 show quantities which are not only relatively very low, but nearly equal. During 1902 and a part of the following year the smoke from the smelter was delivered from four smaller stacks which were erected near the center of the plant. But in June, 1903, the smelter was shut down until late in September in order to permit certain modifications to be made, chief among them being the final work of construction upon the present high stack and extensive settling flue. At the time these samples were collected, one from a haystack and the other of grass from the open field, the smelter had barely begun operations after the summer's inactivity, so that the two samples had been exposed to smoke only during the period of growth until the time of the closing down of the smelter in June, and both were exposed equally long. Sample 8 shows the result of an added exposure of over a month during the dry season of the year. The moss sample from the same locality gave a remarkable result which is to be explained only on the assumption that owing to its peculiar matted growth the moss may have collected the arsenic which fell upon it like a natural filter, and held on to it from the previous year. During the year 1904 no collections were made, though the hay samples taken in the early part of 1905 were from the 1904 crop. The average amount of arsenic in these hay samples collected up to May, 1905, is 41.9 parts per million, while the average of the results for grass is 120.4.

For the year 1905 a noteworthy sample is that of grass (No. 30) from Garrison, thirty-five miles north of the smelter, which carried 35 parts of arsenic trioxide per million. Two samples (Nos. 71 and 72) collected in October of the following year from the same locality carried 29 and 21 parts, respectively, per million. The former sample was old grass collected in May, at which time the grass from the preceding year usually attains its maximum content of arsenic.

It must be admitted that, whatever the amount of arsenic discharged daily with the smoke, we have, without further evidence, no satisfactory

measure of its distribution. If arsenic and copper and other toxic constituents of smelter smoke were not to be found in the soil, their appearance in the vegetaton of the smoke zone could be attributed at once to atmospheric deposition. But it may be claimed that the arsenic and copper found in these samples are not deposited from the smoke stream, but absorbed from the soil itself. It is a fact that growing plants may absorb small amounts of copper from the soil, and a review of the literature would seem to leave no doubt that the same is true, in a very slight degree, for arsenic.

Voelcker[1] experimented with grass grown on soils to which arsenical superphosphate had been added, and Hehner, who made the analyses for him, found on an average 0.0045 grain of arsenic per pound of straw (0.7 part per million). Swedes under the same conditions gave no arsenic in the bulbs, and in one case only 0.02 grain per pound of dried tissue (2.8 parts per million) in the leaves and stems. Barley straw grown on soil manured heavily with superphosphate containing 0.5 per cent. arsenic trioxide carried 0.007 grain per pound (1 part per million) while the leaves of swedes and mangels grown on ordinary soils containing about 0.0002 per cent. of arsenic trioxide were found to contain 0.002–0.004 grain of arsenic per pound (0.3 to 0.6 part per million). Angell[2] analyzed a large variety of cereals and table vegetables which were grown on soil to which superphosphate carrying 0.5 per cent. of As_2O_3 was added. Of thirty-two samples examined twenty-two showed not a trace of arsenic while the rest are reported as containing slight traces. Since, however, only an acid extract of the plant in dilute hydrochloric acid was made, with no effort to destroy organic matter before adding it to the Marsh generator, and since only fifteen minutes were allowed for the arsenic mirror to appear, the results are open to very serious question. Gautier[3] found arsenic in many vegetable foodstuffs; in wheat (0.000,007 per cent.), bread (0.0000071 per cent.), and in potatoes (0.000,0112 per cent.), but not a trace in cabbage and beans. He also claims to have found it in marine and fresh water algae.

Copper in traces has been shown repeatedly to be present in plants grown on coppery soils. In fact the occasional presence of copper in plants has been admitted for nearly a century.[4] Verdrödi[5] found notable amounts of copper in buckwheat (0.87 per cent. CuO), maize (0.06–0.39 per cent.) and other cereals. These results, however, have been criticized

[1] *Report Royal Arsenical Commission*, Vol. II, p. 174.

[2] *Ibid.*, p. 10.

[3] Gautier, *Compt. rend.*, **139**, 101 (1904).

[4] See Meissner-Schweigg, Journal, **17**, 340 (1816); Phillips, *Ann. chim. phys.* [2], **19**, 76 (1821).

[5] Verdrödi, *Chem. Z.*, **17**, 1932 (1894); and **20**, 399 (1896).

by Lehmann,[1] who points out that they are ten times those obtained by Tscherch from soils very rich in copper, and justly criticizes the method adopted by Verdrödi for the estimation of copper, *viz.*, ashing the plant, extracting the residue with nitric and hydrochloric acids, precipitating with hydrogen sulphide, and without further treatment weighing the precipitate as copper sulphide. Lehmann's own results, however, show that minute quantities of copper may be present in certain plants which subsist on a soil containing copper salts.

There are good reasons for believing that the values given for arsenic and copper in the previous table are not due to absorption from the soil. Plants do not absorb so much arsenic or copper as is there shown. The writers have grown cereals on several soil samples which were collected in the Deer Lodge Valley. These were taken outside the range of the smelter smoke and planted to barley and timothy. In no case have they found more than 0.0002 per cent. of arsenic trioxide in the matured plants, where values as high as 0.0263 per cent. had been obtained from grass grown on the same soil five miles from the smelter. Moreover, above everything else the length of time the plant is exposed to the free atmosphere in the smelting district is the determining factor in connection with its arsenic content. A few cases illustrating this have already been cited in connection with some of the earlier results, and many others could be selected. Nos. 53 and 61, samples of wild lily-of-the-valley, were collected by one of us from the same spot about one and three-quarter miles from the smokestack and in a section over which the smoke blows much of the time in the summer months. The first one was cut July 3rd and the other August 14th, or six weeks later. During this time the arsenic content of the plants increased from 583 to 682 parts per million. At the same time these were taken a kind of wild grass (*agrìpìrons dìvergens*) growing at the same place was sampled. These are designated as Nos. 49 and 62. When the first of these was collected the grass was already dead, so the increase in arsenic trioxide from 293 to 482 parts per mllion cannot be ascribed to processes of absorption from the soil. Nos. 44, 66 and 73 are meadow grass samples taken from the same field in the months of July, September and November, respectively. The July sample, covering the period of most rapid growth and most frequent rainfall, carried 12 parts of arsenic trioxide per million. The September sample more than covered the rest of the growing period and carried 34 parts, while the November sample carried 121 parts per million, thus collecting an added 87 parts after all growth had ceased.

A striking proof that the arsenic is deposited from the smoke was found by a study of the wind currents. The Mill Valley district southwest of the smelter is the one toward which the smoke blows most during the early

[1] *Arch. Hyg.*, **24**, 3; and **27**, 1 (1896).

summer, while late in August the air currents begin to go northward down the Deer Lodge Valley, and from this time until the snow covers the ground the greater part of the smoke blows in this direction. The analyses show that the grass of Mill Valley contains more arsenic than any other district during the early summer. Thus samples 48, 50, 51, 52, 53 and 58, which were gathered in July, 1906, contained respectively 157, 359, 460, 293, 583 and 431 parts of arsenic trioxide per million. North of the smelter, sample 12, taken in July 1906, from the Bliss ranch, contained 18 parts, one taken in September 33 parts, and one taken in November 73 parts of the trioxide per million. In 1905 the Bliss grass in June contained 67 parts, in September 61 parts, and in February, 1906 (grass of the season of 1905) it contained 180 parts per million. Hay from the same ranch cut in August, 1904, contained only 30 parts to the million, while by the next April the grass in the same field had increased its arsenic content to 263 parts. During 1906 the Para ranch gave 12 parts in July, 34 parts in September, and 121 parts in November. There is, of course, some objection to a comparison of the grass with the hay, since a certain portion of the arsenic of the latter is shaken off by the cutting and stacking. Even with the grass it is difficult to obtain the original arsenic content, since the sample must be cut, put into containers, and transported to the laboratory.

These results show very plainly that the greatest accumulation of arsenic generally occurs after the period of growth is ended and the plant is dead. There is little doubt that the rains during the early summer wash much of the arsenical deposit from the vegetation, while in winter the grass is protected by snow. The most favorable time then for the arsenic to accumulate on the tissue is during the late summer and fall; and during that period, in fact when absorption through the roots is out of the question, since when the grass is dead the accumulation is most rapid.

That this is deposited arsenic rather than absorbed arsenic is evidenced further by the fact that by shaking dry hay or grass grown in the vicinity of the smelter a finely divided dark-gray powder, running notably higher in arsenic than the tissue from which it came, is obtained. Various samples of this dust were collected by shaking the hay or grass on a fork over a glazed cloth and separating leaves and fragments of the tissue by means of an 80-mesh sieve. This dust accumulates in quantity on the floors and rafters of hay lofts and in the mangers of feeding barns where it can be swept up in large amounts. Several samples of dust were also obtained from parts of threshing machines and analyzed for arsenic. Complaints are often made by men working on these machines that the thresher dust from grain in the smoke zone irritates the skin and the mucous membrane of the eyes and nasal passages.

TABLE III.—ARSENIC IN DUST FROM HAY AND GRAIN.

No.	Year.	Month.	Sample.	Direction from smelter.	Distance from smelter.	As_2O_3. Per cent.	As_2O_3. Parts per million.	CuO. Per cent.	Farm.
1	1905	June	H.[1] Dust	N. E.	4.5	0.0987	987	0.5320	Para
2	1905	June	"	"	4.5	0.0969	969	0.5600	"
3	1905	Apr.	"	"	4	0.4380	4380	0.7430	Staffanson
4	1905	Apr.	"	"	4	0.5140	5140	0.7970	"
5	1905	Oct.	T.[2] Dust			0.0887	887		Bowman
6	1905	Oct.	"			0.0594	594		Perkins
7	1905	Oct.	"			0.0448	448		Watts
8	1905	Oct.	"			0.0410	410		Day
9	1905	Oct.	"			0.0941	941		Jones
10	1906	July	H. Dust	E.	1.5	0.3526	3526		Lappin
11	1906	Nov.	"	S. E.	2	0.9190	9190		Allen

These values are uniformly high, the richest of the hay dust samples exceeding any of those for the plant tissues many times over. The thresher dust samples run lower, due in part at least to the fact that the conditions under which that dust was deposited are more apt to cause a loss in arsenic and a concentration of the heavier silicious dusts. The samples of hay dust from the Para farm were collected from the stack from which hay samples 20 and 31 were taken. The hay averaged 87 parts of arsenic trioxide per million, while the dust shaken from it averaged 978 parts. The dust from the Staffanson hay contained 7700 parts of arsenic trioxide per million, while the hay itself carried 261 parts. In the case of Lappin's hay the dust carried 9190 parts and the hay 50 parts per million. Such results indicate clearly that the arsenic is deposited on the surface of the plant and is not distributed throughout the tissue.

A contention which might be raised is that this dust is soil which has been blown upon the hay, or which adhered to it during the process of curing in the field. Some representative analyses of soil taken to a depth of three inches are given in the following table:

TABLE IV.—ARSENIC IN SOILS.

Farm.	Distance.	Per cent. As_2O_3.
Staton	2 miles S.	0.0019
Callan	3 " S. W.	0.0029
Para	4.5 " N. N. E.	0.0043
Bliss	5.5 " "	0.0061
Staffanson	3 " "	0.0107

The Para hay dust then carried 22.7 times as much arsenious oxide as did the soil. The Lappin hay dust carried 483 times as much as the soil sample from the adjoining Staton farm; and the Staffanson hay dust contained 72 times as much arsenic as the soil upon which it grew. It is

[1] H = Hay.
[2] T = Thresher.

extremely unlikely that dust from the soil is any large contributor to the quantities of arsenic found in the hay dust. Rather would it appear more reasonable to assume that in so far as the soil is present it is a diluent which diminishes the percentage of arsenic. Originally the soil of this district does not seem to have been arsenical. The top three inches of uncultivated soil will usually afford small quantities of arsenic which rapidly vanish at greater depths. A sample of top soil taken from underneath a well built log house erected long before smelting operations began in that valley carried only a trace of arsenic, while soil from an adjoining field was found to contain 0.0107 per cent. in the top three inches. Soil which had never been plowed contained no arsenic whatever at depths of from twelve to fifteen inches, so the arsenic present in the top soil would seem to be due wholly to the smelter emanations.

Samples of snow were scraped from the surface at a time when the ground for miles was covered with a sheet which had not yet been disturbed by the wind. Considerable amounts of soluble arsenic were found, the arsenic being dissolved in the water formed when the snow melted. The appended table gives the analytical results obtained:

TABLE V.—ARSENIC IN SNOW.

Date, 1906.	Farm.	Distance and direction.	Weight of snow grams.	Sq. ft. surface area.	Time exposed.	As_2O_3 per sq. ft.	Per cent. of dust.
2–5	Para	5 miles N.	925	6.228	17 days	0.00306	0 1130
2–5	Williams	4 " N.	955	12.6	17 days	0.00026	0.1690
2–5	Bliss	5.5 " N.	...	...	17 days	0.00040	0.2810
3–18	Callen	3 " S. W.	808	13.45	3 days	0.00057	.....
3–18	Bliss	5.5 " N.	604	6.72	3 days	0.00058	.....

The figures in the column "Per cent. of dust" include the percentage of soluble arsenic calculated as if it were a component of the water-insoluble dust.

Early in the fall of 1905 vaselined cloths, each presenting a surface of three to eight square feet, were exposed at several points near the smelter. One was fastened to each side of a board tablet, somewhat larger than the cloth, which was set up on poles about twelve feet above the ground and broadside to the direction of the smoke stream at that place. Thus one vaselined cloth faced the smelter and the other faced in the opposite direction. In one case (No. 2) a cloth was stretched horizontally above the other two with its vaselined surface upward. Samples 1 and 2 were set up September 5th and taken down November 21, 1905. No. 3 was set up October 1st and taken down March 18th, but the vaselined surface was frozen hard and smooth for most of the winter and its efficiency as a collecting medium thus greatly decreased. The following data were obtained from this experiment:

TABLE VI.—ARSENIC IN VASELINED CLOTHS.

No.	Farm.	Direction from smelter.	Distance from smelter.	No. days exposed.	As_2O_3 per sq. ft. of cloth. Facing upward, gram.	Facing smelter, gram.	Facing away, gram.
1	Bliss	N.	5.5	77	...	0.00052	0.00024
2	Para	N.	5.0	77	0.01194	0.00700	0.00083
3	Staton	S. E.	5.0	169	...	0.00327	0.00051

The results admit of only one interpretation, which is that the smelter smoke is the source of the arsenic found in such excessive amounts in the vegetation of the region about Anaconda. The question of whether this is a condition for which there is no remedy is difficult to answer. It is doubtful whether the present limited water supply would permit of the installation of wash towers, and the large amount of sulphur trioxide in the smoke would be destructive to a bag-house system. With its present high temperature and velocity the smoke must carry most of the arsenic out of the stack. In spite of the use of dry filters and wash towers and a consequent low velocity of the smoke, in an effort to meet the requirements of the amended Alkali Acts of 1892, the average escape of arsenic trioxide from the chimneys of arsenic plants in England for the past five years has been 0.0028 gram (0.041 grain) per cubic foot.[1]

In the thirtieth annual report[2] the Chief Inspector under the Alkali Acts wrote: "The inspection of these works (*i. e.*, arsenic works) had been much called for by residents in the district where they are found, and the necessity for the adoption of remedial measures was shown by the frequent litigation brought about by the alleged destruction of cattle through eating grass said to be poisoned by the arsenic too freely distributed through the air from the chimneys up which it had been carried by the draught. The arsenic driven off by the heat of the roasting furnace was caught and retained as far as possible, in long flues, culverts, and settling chambers, but although these were often of great extent, reaching in one place, a length of 2895 feet, or more than half a mile, and having a capacity of 60,795 cubic feet, yet arsenic was always liable to pass away. In one case a test of the chimney gases showed the presence of as much as 7.40 grains of arsenic trioxide in a cubic foot of gases passing into the air, and small flakes of it were seen falling continually in a mild snow-shower." The average escape of arsenic trioxide per cubic foot of chimney gases from plants provided with wash-towers, or with dry filters made by packing large chambers with brushwood, for each year since 1896 was as follows:

1896	0.080 grain
1897	0.086 "
1898	0.098 "

[1] Annual Reports Chief Inspector under Alkali Acts 1902–6.

[2] 30th Annual Report under Alkali Acts (1893), p. 91.

1899	0.074 gram
1900	0.094 "
1901	0.083 "
1902	0.049 "
1903	0.039 "
1904	0.053 "
1905	0.036 "
1906	0.030 "

These results attest the difficulty of removing all the arsenic from chimney gases even where, as in many of the plants referred to above, the furnace gases are cooled by wash-towers and the velocity of the smoke is reduced by extensive settling chambers. The smoke proceeding from the smelter at Anaconda on the basis of results presented in the first paper carries about 0.200 grain per cubic foot, a considerable velocity even in the settling chambers and a chimney temperature of 180° both interfering strongly with the deposition of the arsenic. The quantity which is given off under the present smelting conditions is not likely to be reduced except by the use of a less highly arsenical ore. As the ore supply for the Anaconda plant in drawn entirely from the mines of the Butte district and the arsenic content of these ores seems to be constantly increasing as greater depths are reached, the prospect of finding a ready solution of the problem is not encouraging. The great value of the products lost in the smoke, as shown by the first paper of this series, should encourage smelter companies to conduct extensive experiments with a view to the mitigation of this evil.

TABLE VI.[1]

No.	Collected.	Sample.	Source.	As_2O_3. Per cent.	As_2O_3. Parts per million.
1	July 12, 1907	Grass	Everett, 300 ft. S.E. from smelter..	1.3000	13,000
2	July 12, 1907	Grass	Everett, ¼ mile S. E. from smelter.	0.9400	9,400
3	July 12, 1907	Poplar leaves	Everett, 50 ft. W. from smelter....	4.4000	44,000
4	July 12, 1907	Grass	Everett, 50 ft. W. from smelter....	0.2300	2,300
5	July 12, 1907	Grass	Everett, 100 ft. N. from smelter...	0.2300	2,300
6	July 12, 1907	Grass	Everett, ¼ mile N. from smelter...	0.0420	420
7	Aug. 11, 1906	Sunflower leaves, ¼ mile from Murray smelter, Utah		0.1072	1072
8	Aug. 11, 1906	Grass, ½ mile from Highland Boy smelter, Utah...		0.0062	62
9	Aug. 12, 1906	Alfalfa, 1 mile from Highland Boy smelter, Utah.		0.0038	38
10	Aug. 12, 1906	Grass, 2 mile from Bingham smelters, Utah.....		0.0021	21
11	Aug. 12, 1906	Grass, 1 mile from Bingham smelters, Utah.....		0.0045	45
12	Aug. 12, 1906	Milkweed, 3 miles from Highland Boy smelter, Utah		0.0027	27

Incidental to this work in connection with the smelter at Anaconda samples of plant tissue have been collected from two other prominent

[1] A large number of grass samples from other smelter districts have been analyzed since the completion of this paper. Many of these contain arsenic in large quantities.

smelting centers, from Everett, Washington, about thirty miles north of Seattle, and from the region a few miles south of Salt Lake City, Utah, where several large smelters are in operation.[1] At both of these places complaints of injury to live stock have arisen from time to time. Only a few of these samples have been analyzed with the above results.

The writers wish to express their indebtedness to Dr. John Maxson Stillman for suggestions in regard to this work.

THE UNIVERSITY OF MONTANA, MISSOULA, MONTANA, AND STANFORD UNIVERSITY, CALIFORNIA,
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THE CHRONIC ARSENICAL POISONING OF HERBIVOROUS ANIMALS.[2]

(PAPERS ON SMELTER SMOKE, THIRD PAPER.)

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The two outbreaks of supposed arsenical poisoning which have led to the most investigation from a scientific standpoint, are the one in Manchester, England, in the year 1900, and that in the district surrounding Anaconda, Montana, during the year 1902-1903. The former was confined to human beings, the latter almost entirely to cows, horses, and sheep. As yet very few data have been obtained to show whether or not the effects of the arsenic in the latter case extended to the human beings who resided in the district.

During the latter part of November, 1902, it was the fortune of one of us to travel over about one hundred square miles of the territory surrounding the new Washoe smelter at Anaconda. At that time the carcasses of several hundred animals that had recently died lay scattered over various ranches of the valley, and one ranch was visited where approximately sixty carcasses, mostly horses, were seen in a group in one corner of the field. A very large number of the animals were dissected, and practically all of them gave evidence of arsenical poisoning, either acute or chronic.

As has been explained more in detail in a former paper, what was called the "Old Works" had been in operation for many years on the north side of the valley of Warm Springs Creek, in which the city of Anaconda is located. In January, 1902, smelting operations were transferred to the "New Works," which are located on the south side of the same valley, on a ridge extending down from the foot-hills. This ridge projects into the Deer

[1] See Ebaugh, Gases *vs.* Solids, THIS JOURNAL, 29, 951, 970 (1907).

[2] At the New York meeting of the American Chemical Society, December, 1906, W. D. Harkins presented a similar paper including only his own work. The first paper of this series deals with the amount and character of the smoke given off by the smelter, and the second treats of the arsenic content of the vegetation.

Lodge Valley in such a way that much more of the smoke from the smelter was blown across or into the valley than during former years.

Although the smelter was in operation during the whole year, few cases of serious sickness among live stock were noticed until September, from which time the number of deaths increased rapidly until November, when a maximum was reached. This is easily understood when the facts of the case are considered as presented in the second paper of this series.[1] The fresh grass of the spring has little time to accummulate arsenic from the air, and the summer is a period of rapid growth and frequent rains; in the autumn comes a dry period during which there is no plant growth, so this is the most favorable period for a rapid increase in the amount of solid substances adhering to the leaves and stems of the plant. During this dry period, the farmers were forced to drive or ship a great number of animals from the district, and those remaining were stabled and fed upon hay. The owners had found from their experience with the symptoms exhibited by the animals, that the disease was greatly moderated by changing the diet from grass to hay. This was explained by the much smaller amounts of arsenic found in the latter.[2]

In 1903 the smelter company had built the great flue and stack described in the first paper[3] in order to prevent the escape of the arsenic. In accordance with an agreement entered into with the farmers, the smelter was shut down from July 1st to September 30th of this year, and when the plant was started on the latter date the smoke was supposed to no longer scatter poisonous substances over the valley, since it was passed through the flue intended for its purification. During the summer and autumn of this year there were very few cases of death among the animals of the valley and it was believed by the residents of the valley that there would be no more cases of sickness due to arsenic.

Two interesting exceptions were investigated in cases where the farmers thought that arsenical poisoning had occurred. A drayman in the city of Anaconda purchased a load of hay, supposed by him to have been grown during the year 1903. After feeding the hay to his horses for about a week one of them sickened and died, the most marked symptons before death being recurrent convulsions. A post-mortem examination showed the usual inflamed condition of the stomach, and the presence of a number of small ulcers, resembling those frequently observed in cases of arsenical poisoning. An analysis of the hay gave 0.0285 per cent. (285 parts per million) of arsenic trioxide. Various tissues of the animal were also analyzed and the liver found to contain 1.30 milligrams of arsenic trioxide to one hundred grams of tissue (13 parts per million). It seemed improb-

[1] THIS JOURNAL, preceding paper.
[2] Table 3; or Table I, preceding paper.
[3] THIS JOURNAL, 29, 971–3 (1907).

able that hay which contained so much arsenic could have been grown in the year when the smelter was closed for the three summer months, and upon investigation it was found that the hay had been grown about three miles north of the smelter during the preceding year.

In October, a sheep owner who lived about twenty-eight miles from the smelter, and in a small valley somewhat protected from the smoke by an intervening range of hills, found that his grass was becoming exhausted. He rented a low field lying approximately fifteen miles northeast of the smelter, and drove his three thousand five hundred sheep from his home to this field, upon which there was a large amount of grass. After pasturing there for a week, a number of the sheep became sick, and the neighbors advised the owner to drive the flock to a feeding place farther from the smelter. On the way home five hundred sheep died, but during the next four weeks the mortality diminished. The total loss was six hundred and twenty-five animals. The case was investigated by the state veterinarian, Dr. M. E. Knowles, who decided that the sheep had died from acute arsenical poisoning. The four samples submitted by him for analysis gave the following results:

TABLE I.

Number.	Organ.	Parts As_2O_3 per million.
1	Stomach	3.1
2	Stomach	Trace
3	Stomach and liver	3.0
4	Stomach and liver	4.0

Claims were made that the sheep had died from poisoning caused by the alkali of the soil. A complete analysis of the soil, and a partial analysis of the stomachs of the sheep, showed that this was not true. It is a fact that the soil was high in the salts of the alkalis, containing 0.70 per cent. soda (Na_2O), 1.38 per cent. potash (K_2O), 0.40 per cent. sulphuric acid (SO_3), 0.00306 per cent. arsenic trioxide, 0.0118 per cent. copper, together with lead, a trace of antimony, etc.

A visit was made to the field to see if the cause of the death of the sheep could be determined. The grass was cropped very close to the ground, and over the lower part of the field there was a large amount of moss which had been greatly disturbed, presumably by the sheep during their feeding. On analysis it was found that the grass contained fifty-two, and the moss four hundred and five parts of arsenic trioxide in a million. It was therefore a reasonable assumption that the sheep had been poisoned at first by eating the grass, and in a greater degree by eating the moss at a time when the grass was nearly exhausted. It is probable that the sheep were very hungry when they first reached the field as they had lived for some time upon a meagre food supply.

There were no more complaints of serious damage from the farmers, so

far as the effects of arsenic were concerned, until late in the autumn of 1904. It is true, that, while the effects of sulphur dioxide upon the plants had been moderated on the average, it had become more severe at many points some distance from the smelter. The charge began to be made by the farmers that the same was true of arsenic, and that symptons of arsenical poisoning had again manifested themselves in spite of the use of the big flue and stack. Chemical investigations were actively renewed in January, 1905, and have continued up to the present time. The results of the analyses of smoke and forage have been given in the previous papers of this series. A reference to these will show that enormous quantities of arsenic were thrown out by the high stack, and that large quantities were present on the vegetation.

Autopsies of a large number of animals were made, and many of the samples analyzed. Great care was taken with all of the analyses so that quantitative results of considerable accuracy might be obtained, and some of the precautions used will be described in a subsequent paper. The methods were first tested by analyses upon known amounts of arsenic. Various substances were used in the decomposition of the tissue, but the methods of Fresenius, von Babo, and Chittenden-Donaldson were adopted almost exclusively. All reagents were scrupulously purified from the most minute traces of arsenic, and were tested very frequently during the course of the analyses. All of the glassware, glass tubes, rubber tubes, porcelain-ware, etc., were tested to see if they would give traces of arsenic when used in the manner necessary for the tests. Berlin porcelain was used to the exclusion of glassware, except for the Marsh apparatus, which was made of Jena glass.

A modified Chittenden method which was much used in cases where little fat was present, consisted in putting 100 grams of the sample into a large casserole, and adding 100 cc. of nitric acid. The mixture was stirred frequently until it had become liquid, and was then heated on an asbestos board which rested on an electric stove. After heating for a half hour longer the solution was cooled, and thirty cubic centimeters of concentrated sulphuric acid added. The solution was heated until it began to turn brown, and then the steam of a dropping funnel was introduced through a hole in the watch glass cover, and nitric acid allowed to drop into the hot solution just rapidly enough to keep it from turning dark. After this addition has been kept up for some time, the solution could be evaporated (while adding nitric acid drop by drop) until the fumes of sulphuric acid appeared, without a blackening of the solution. A part of the sulphuric acid was then evaporated, nitric acid being occasionally added. The cooled solution was diluted and re-evaporated in order to remove oxides of nitrogen which might be present, and the cooled and diluted solution used for the determination of the arsenic by a modified Marsh method. The

generator was kept active for six hours, stannous chloride being used to increase the activity of the zinc. It was found that this length of time was essential where weighable quantities of arsenic were determined. The best results were obtained by the use of a special fire-brick furnace with four very large burners. A second hard glass tube lying in a second furnace was connected with the first in order to test the completeness of the decomposition of the arsine, and arsenic was always found in this tube in cases where action in the generator became at all rapid.

The results of the analyses of a part of the animal samples are given in Table 2.

TABLE 2.—AMOUNTS OF ARSENIC IN THE TISSUES OF ANIMALS.

No. and organ.	Date.	Animal.	Distance.		Parts As_2O_3 per million.
	1902				
1 L	Sept.	Horse	3	NW	4.7
2 L	Sept.	Horse	2	SSE	1.1
3 L	Sept.	Horse	5	SE	2.8
4 L	Sept.	Horse	5	SE	0.8
5 L	Sept.	Cow	3	E	11.3
6 L	Sept.	Calf	3	S	6.2
7 L	Sept.	Calf	1.5	S	0.4
8 L	Sept.	Calf	1.5	S	0.3
9 L	Sept.	Steer	3	NE	8.6
	1903				
10 S	Oct.	Sheep	15	NNE	3.1
11 S	Oct.	Sheep	15	NNE	Trace
12 L & S	Oct.	Sheep	15	NNE	0.7
13 L & S	Oct.	Sheep	15	NNE	4.0
14 L	Oct.	Horse	1.5	NE	13.0
	1905				
15 L	Jan.	Filly	3	N	0.01
16 Lu	Jan.	Geld	5	E	7.1
17 S	Jan.	Geld	2	SW	0.01
18 L	Jan.	Cow	6	SE	3.3
19 L	Jan.	Geld	4.5	NNE	35.0
20 K	Jan.	Mare	14	NNE	13.3
[1]21 L	Jan.	Colt	2	S	2.6
22 L	Jan.	Cow	3	SW	1.6
[1]23 L	Jan.	Cow	3	SE	2.1
24 L	Jan.	Cow	5	NE	11.9
25 L	Jan.	Cow	5	NE	10.3
26 L	May	Steer	13	NNE	0.01
27 L	May	Cow	6	N	0.01
28 L	Nov.	Cow	13	NNE	10.00
29 L	July	Cow	2	S	7.4
[1]30 L	Jan.	Sheep	8	N	0.01

[1] The shoulder of colt 21 was covered with a green fat which contained 288 parts of copper to the million. Sample 30 L contained 592 parts; and sample 23 L, 88 parts of copper to the million.

TABLE 2 (*Continued*).

No. and organ.	Date.	Animal.	Distance.		Parts As_2O_3 per million.
31 L	Jan.	Sheep	3	N	6.8
32 L	Jan.	Calf	2	S	1.5
33 L	Jan.	Calf	3	SW	6.5
34 L	Feb.	Calf	2	S	1.3
	1906				
35 L	Nov.	Geld	3	S	6.0
36 L	Oct.	Geld	4	N	3.4
37 L	Aug.	Mare	4.5	NE	4.4
38 L	Aug.	Geld	1.7	SSW	3.9
39 L	Aug.	Horse	5	NNE	16.1
40 L	Aug.	Horse	5	NNE	9.5
41 L	Jan.	Mare	5	NNE	1.3
42 L	Sept.	Geld	4.2	NNE	14.8
43 K	Jan.	Mare	15	N	2.1
44 L	Jan.	Mare	15	N	8.7
45 L	Jan.	Geld	10	NNE	7.6
46 L	Jan.	Geld	3	N	5.3
47 L	Feb.	Filly	4.5	NNE	3.1
48 L	Feb.	Filly	5	N	17.8
49 L	Feb.	Mare	4.5	NNE	8.7
50 Br	Feb.	Mare	4.5	NNE	4.5
51 H	June	Filly	4.2	NNE	460.0
52 L	Mar.	Horse	1.5	S	20.7
53 L	Aug.	Mare	12	NNE	4.99
54 B	Aug.	Mare	12	NNE	20.67
55 L	Sept.	Horse	4.5	NNE	Trace
56 L	Sept.	Mare	6.5	SE	52.5
57 L	Sept.	Geld	4.5	NNE	3.3
[1]58 K	Feb.	Colt	4.5	NNE	19.8
59 L	Feb.	Colt	10	NNE	Trace
60 L	Feb.	Colt	4.5	NNE	25.5
61 L	July	Colt	3	NNE	31.7
62 L	July	Colt	2	S	4.4
63 L	Nov.	Colt	9	NNE	2.6
64 L	Oct.	Colt	2	S	4.7
65 L	Aug.	Colt	8	NE	2.2
66 L	July	Colt	8	NNE	1.1
67 L	Feb.	Cow	10	N	11.8
68 L	Feb.	Cow	3	SSE	33.8
69 L	Nov.	Cow	13	NNE	10.0
70 L	July	Cow	3	N	14.2
71 K	July	Cow	3	N	6.2
72 L	July	Cow	3	N	63.12
73 L	Nov.	Cow	3	SSE	9.2
74 U	Nov.	Cow	3	SSE	16.0
75 L	Nov.	Cow	10	NNE	1.2
76 L	Nov.	Cow	4.2	NNE	10.4
77 L	Jan.	Steer	5	E	5.4
78 L	Oct	Calf	1.7	SW	16.2

TABLE 2 (*Continued*).

No. and organ.	Date.	Animal.	Distance.		Parts As_2O_3 per million.
79 L	Feb.	Calf	3	SSW	6.3
80 L	Jan.	Sheep	10	N	8.9
81 L	Aug.	Sheep	4.2	NNE	5.0
82 L	Sept.	Pig	1.7	SSW	Trace

L represents a sample of the liver; B, of the bone; Lu, of the lungs; U, of urine; H, of hair; K, of kidney; Br, of brain; S, of stomach. The animals represented by samples 1 to 42 were more emaciated on the average than those represented by samples 43 to 82.

The number of parts per million multiplied by seven-tenths gives the number of grains of arsenic trioxide to one hundred pounds of tissue. In this way a comparison may easily be made with the recommendation of the Royal Commission on Arsenical Poisoning:[1]

"In our view it would be entirely proper that penalties should be imposed under the sale of Food and Drugs Acts upon any vender of beer or any other liquid food or of any liquid entering into the composition of food, if that liquid is shown by an adequate test to contain 1/100 of a grain or more of arsenic in the gallon; and with regard to solid food—no matter whether it is habitually consumed in large or small quantities, or whether it is taken by itself (like golden syrup) or mixed with water or other substances (like chicory or 'carnos')—if the substance is shown by an adequate test to contain 1/100th grain of arsenic or more in the pound."

According to this recommendation a large number of the samples of liver given in Table 2 would be considered as deleterious when taken as food by human beings, and in one case a cow's liver contained forty-three times the maximum amount allowed in food by the commission. Flesh and also milk were found which exceeded the limit prescribed by the commission.

The livers of animals, according to Table 2, contained from a trace to 63.12 parts of arsenic trioxide to one million parts of tissue. The maximum number was obtained in a case of acute poisoning which occurred about three miles north of the smelter. This seems a strange case when it is considered that, although the grass of the ranch has usually contained a large amount of arsenic, at the time the cow died the percentage was relatively low, being between thirty and forty parts to the million.

An effort has been made to trace a relation between the quantity of arsenic ingested with the food, and that contained in the livers of the animals, but this has been impossible. It is true that the amounts of arsenic are larger on the average in cases where the animals were kept close to the smelter, but it is obvious that the condition of the animal is the more important factor in determining the amount of arsenic retained by the tissues.

[1] Final Report Royal Commission on Arsenical Poisoning, p. 50 (1903).

The amounts of arsenic present in the organs of the animals is in many cases small, yet no smaller than might reasonably be expected in chronic arsenical poisoning following the repeated and regular administration of moderate doses of arsenic. Before the time of this investigation, very little experimental work had been done on horses and cattle in which accurate analyses had been made of the organs following arsenical poisoning. In a case reported by the Russian Minister of the Interior, the liver of a cow which had been fed considerable amounts of arsenic for a period of six months, contained 0.13 part of arsenic per million. Spallanzani and Zappa[1] fed a cow from 0.4 to 0.5 gram (6 to 8 grains) of arsenic trioxide daily for 44 days and the following results in parts of arsenic per million were obtained from an analysis of the viscera:—stomach, 19; liver, 11; kidneys, 4.5; spleen, 7.6; lungs, 3; muscles, 3.8.

In order to see how the results of Table 2 would compare with those obtained from animals killed by arsenic, and also in order to secure data as to the poisonous dose, horses were fed upon arsenic in different forms. The doses given were large as the time for the experiments was very short. A horse was fed upon flue dust containing a total of 20.65 per cent. of arsenic calculated as trioxide, and 17.89 per cent. of soluble arsenic, also calculated as trioxide. Considering only the soluble arsenic, the horse was fed two grams of arsenic trioxide for eighteen days in addition to hay containing about 0.0030 per cent. In the liver was found 3.5 parts, and in the kidneys 18.0 parts per million, an amount for the liver which was less than the average of the values given in Table 2. A second horse was given 2.8 grams (0.1 oz.) of arsenic trioxide in two doses, on the first day mixed with bran, and on the second ingested as a drench. On the fourth day the animal died, and on analysis the liver was found to hold 8.7 parts per million. A third horse died on the third day after having been given two doses of 7.5 grams each, one on the first, and one on the second day. The liver contained 12.2 parts, while that of a sheep which had been fed arsenic for some weeks contained 11.9 parts to the million.

In taking samples during the first few years of the case, the more emaciated animals were usually selected, but beginning with January, 1906, a larger number of those that were fat and in a seemingly good condition were chosen. The result of this change of policy is shown in the table, where the average content of arsenic for 1906 is much higher than for previous years.

The elimination of arsenic probably begins very early and persists during the whole period of its absorption. In the human subject it often appears in the urine within five hours after ingestion, and may continue to be eliminated for thirty days after the last dose is taken. This is unusual, however, fifteen days usually sufficing to remove almost all of the arsenic

[1] *Annal di Agricoltura*, 131, 25.

from the human system. The difficulty in finding in the tissues any considerable amount of arsenic—an amount for example, sufficient to prove on the basis of a chemical analysis alone that death was due to arsenical poisoning, lies here. And where the case is one of chronic poisoning extending over a long period, and caused by a fairly constant amount of the poison being ingested daily, the isolation of an amount approximating a toxic dose is often impossible, simply because a really toxic dose was never taken at one time, and what was taken was partly excreted by the kidneys even before its absorption from the stomach and intestines was complete.

The proof of poisoning is complete, (1) "when the symptons known to be caused by the poison have been observed during life; (2) when the post-mortem examination shows the presence of such lesions as it is capable of producing, and the absence of other causes of death; (3) when the toxic agent is demonstrated to be present in the cadaver or dejecta of the animal poisoned." It is not always possible to present evidence along all these lines, for it has often occurred, even with a poison so prompt in its action and of such certainty of detection as arsenic, that life may be prolonged for a sufficient length of time to permit the total elimination of the poison, and death results from its action by a continuation of the morbid processes which it established. Again one of the symptoms of chronic poisoning through arsenic is loss of appetite, so that often during the last few weeks or days of life, little or no food is taken. Then where the poison accompanies the food, and is proportionate to it in amount as in the cases at issue in this investigation, failure to take any considerable amount of food during the last few weeks of life, stops the ingestion of the poison and allows the system to expel all or nearly all the substance before death ensues. In certain of the cases given in Table 2, animals apparently in a diseased condition were slaughtered. This was true of cow 31, whose liver showed 6.8 parts of arsenic trioxide to the million, or a total of 0.5 grain for the entire organ. It also carried 1.5 grains of copper. Though considerably emaciated, the large quantity of food in the stomach showed that the animal had not lost its appetite, and this was substantiated by the statement of the owner. A sheep from ten miles north of the smelter, on the other hand, though slaughtered, was virtually in a dying condition, and had evidently partaken of but very little food for some time. Only a slight trace of arsenic could be detected in the liver, but a surprisingly large amount of copper was present. Still the animal was undoubtedly suffering from arsenical poisoning, and the reason so little arsenic and so much copper were found is that arsenic is rapidly eliminated while copper is very slowly excreted, being retained mainly by the liver. In some of the cases very large amounts of copper were found in the fat, a part of which had a greenish tinge.

Moderate amounts of arsenic continuously administered, cause an in-

crease in body weight and much increased storage of fat between the muscles as well as around the kidneys. While this is true in general of all animals it is notably true of herbivorous animals. In minute doses arsenic improves the appetite and increases both the motions and secretions of the stomach and duodenum; and since there is no considerable accumulation of arsenic, due to its rapid elimination through the excretory channels, medicinal or smaller doses may be administered daily over a prolonged period without showing harmful effects.

Reliable data on the subject of the arsenical poisoning of live stock are very meagre, and most of the statements found in the usual text books are so conflicting that a definite conclusion as to what may be considered a fatal dose of arsenic for a horse, cow, or sheep, cannot be reached through them alone. Much of the most reliable work has appeared in the chemical journals.

Spallanzani and Zappa[1] fed moderate amounts of arsenic continuously to a "Durham" cow for 46 days, when death resulted. From 0.5 to 3.0 grams (7.7 to 46.3 grains) of arsenious oxide were administered daily, the dose being gradually increased to the maximum of 3 grams, when the animal died. Spallanzani concludes from this and other experiments that cattle will take without injury, over indefinite periods, doses of 0.5 to 0.7 gram (7.7 to 10.8 grains) of arsenic trioxide per day, and may indeed increase in weight under it. They first show toxic symptoms with doses of 1 gram (15.4 grains) per day. The maximum non-toxic dose for cattle is given as about 0.00015 part of arsenious oxide per day for 100 parts body weight, or 10.5 grains per day for an animal weighing 1,000 pounds.

The results cited in the last paragraph are well in accord with the results of the investigations of the writers as made on the animals of smelter districts. A review of the literature of the subject reveals such great discrepancies in regard to the fatal dose that it is almost impossible to believe all of the results cited. On the one hand, we have the work of Cameron[2] which shows that ten cows were killed by one dose for each cow, of 8.4 grains of arsenic trioxide in the form of sodium arsenite. In contrast with this case, which seems to be authentic, we have the statement attributed to Hertwig[3] that he gave arsenic to eight different horses in doses beginning with twenty grains but increasing to a dram, and continued these doses for from 30 to 49 days with no bad effects, in fact, "the condition was improved."

On account of the unsatisfactory state of the literature of this subject, it was decided to inaugurate further experiments to test the effects of

[1] *Annal di Agricoltura*, 131, 25.
[2] *Analyst*, 1888.
[3] *Veterinarian*, 1843, p. 345.

different doses upon cows and horses. However, at this time it was not found possible to meet the expense of such an undertaking, so the work was done upon sheep.

Results of Work on Sheep.—Four of the healthiest sheep were chosen from a flock of several hundred. They were fed upon local arsenic-free hay at Palo Alto, California, and the doses given in starch capsules as follows:

TABLE 3.

	Dose. Arsenic trioxide.	Weight at beginning.	Form of arsenic.
1.....	0.181 gram twice a day	95 lbs.	Arsenic trioxide
2.....	0.123 gram once a day	87.5 lbs.	Sodium arsenite
3.....	0.055 gram once a day	115 lbs.	Sodium arsenite
4.....	0.021 or 0.090 gram once a day	90.5 lbs.	Sodium arsenite

The results of this experiment are given graphically in Fig. 1. Sheep No. 4 was given daily doses of 0.021 gram for 35 days, when an increase to 0.090 gram was made, because it was believed that upon the smaller dose the sheep would not die before the conclusion of the experiment at the end of ninety days. This was the only sheep that did not die, but that

Fig. 1.—Effect of arsenic trioxide on the weight of sheep.

NOTE.—Curve I is raised ten units of weight in order not to interfere with Curve IV.

death would have resulted soon after the expiration of the time set for the close of the experiment is evident from the curve (*IV*) which shows a rapid decrease in weight toward the end of the period.

The experiment shows that 46 milligrams (0.7 grain) of arsenic trioxide per day, administered in the form of arsenite of sodium, to 100 pounds of body weight, is sufficient to cause the death of a sheep. The perfectly regular way in which the arsenic reacted upon the sheep as expressed in the curves of the body weight, at least suggests strongly that the result was not due to individual susceptibility.

The case of sheep No. 2 was an instructive one. It was given a dose of 0.123 gram per day for twenty-five days, and lived eight days longer before death ensued. No food was taken during the last thirteen days, and practically none for eighteen days, though fresh food was offered three times each day. During the eighteen days the animal was practically in a comatose condition, suffering no pain, and reclining upon its side most of the time. On dissection the intestines were found absolutely empty, since an attack of diarrhea had lasted for eight days, while the stomach was greatly distended and packed with solid food. Digestion had been absolutely suspended for a long time, and decomposition of the stomach lining had already begun. At the beginning of the feeding the animal weighed 87.5 pounds, and at the end 56 pounds, of which eight pounds was undigested food packed in the stomach. A number of the doses of arsenic were found undigested in this organ. To each million parts the liver contained a trace, the tissue of the stomach 3.0 parts, and the brain 4.2 parts, certainly a peculiar distribution of the poison. Evidently little arsenic had gone into the circulation from the stomach for a considerable period, so the liver had been able to eliminate most of the arsenic. The post-mortem appearance of the organs of the sheep, taken as a whole, was that of acute rather than long standing chronic arsenical poisoning.

The question of the amount of arsenic which will kill a farm animal, if fed daily, is a very important one to the chemist who undertakes to investigate the conditions existing in smelter regions. The effects depend so greatly upon the conditions that even after such an extensive investigation as that carried out by the veterinarians, pathologists, bacteriologists and chemists, upon the present case, no very definite statements can be made in regard to this point. A study of Table 1 of the second paper of this series will give some idea of the poisonous dose, for on almost all of the ranches listed, animals have been supposed to die from arsenical poisoning. On the other hand, there is almost no place in the farming district where some of the animals will not survive. As has already been indicated, there is comparatively little sickness during the late spring and summer, but by November a large number of animals are affected, if they are allowed to run upon the pastures.

The following table gives the average amounts of arsenic trioxide in the grasses analyzed during the last three years:

TABLE 4.—AVERAGE AMOUNTS OF ARSENIC TRIOXIDE IN GRASS AND HAY.

	As_2O_3 in parts per million.		Grains to 25 pounds food.	
Year.	Grass.	Hay.	Grass.	Hay.
1905	106	45	18.6	7.9
1906	155	42	21.7	7.4
1907	100	..	17.5	...

The column "Grains to 25 pounds food" is supposed to represent the amount of arsenic taken in a day's feeding, since this is the amount of dry matter in the daily ration for this region. On the average, then, the daily ingestion of arsenic is about 20 grains for grass, and 7.5 grains for hay. The amount varies from a minimum of 1.75 grains for young meadow grass taken two miles south of the smelter, to 271.4 grains for a sample taken in the smelter field one fourth mile from the old low stacks. The average for the grass is interesting in comparison with the statement of Spallanzani and Zappa, that one gram (15.4 grains) per day is the minimum amount which can give rise to the toxic symptoms in cattle.

The farmers claim that animals which are shipped into the valley succumb more quickly than those that have lived for some time in the district, and this is undoubtedly true. It might be assumed that this means the animals able to survive are those of great individual resistance and tolerance with respect to arsenic, an assumption which is true in part; but, in addition to this, there is little doubt that tolerance is gradually established to a certain extent by the use of the poison, as is the case with human beings.

In order to see what proportion of the arsenic in the plants would be soluble in the digestive juices of the animals, and thus act as a poison, two digestion experiments were made. A sample of hay or grass, 300 grams, was digested at 38° C. for two days with a glycerol extract of the mucus lining of the abomasum, the mixture being made acid with hydrochloric acid. Then the liquid was made slightly alkaline with sodium carbonate, digested five days with the glycerol extract of two pancreas glands, and toward the end of the time putrefactive bacteria were added. The results were as follows:

	Grass. 5 mi. N.	Hay. 4 mi. N.
Percentage of soluble As_2O_3	0.0242	0.0058
Percentage of insoluble As_2O_3	0.0019	0.00114
Total per cent. As_2O_3	0.0261	0.0069
Percentage of total arsenic which is soluble	92.6	83.6

The greater amount of arsenic is undoubtedly in a poisonous form.

The Distribution of Arsenic in the Organism.—Several animals were sampled in such a way that portions of nearly every organ were taken, but only one set of data will be presented—for a case in which the distribution

seemed normal in comparison with our other results, although the amount of arsenic is lower than the average. On November 4, 1906, a horse was killed and sampled. In general condition, the animal was unthrifty, and its coat was very rough. The clinical symptoms were redness in the stomach and intestines, congestion of the lungs and pleura, congestion of the brain and bladder, slight congestion of the kidneys, catarrh of the intestines and an enlarged spleen. The results of the analyses of the organs are presented in Table 5.

TABLE 5.—THE DISTRIBUTION OF ARSENIC IN THE TISSUES OF A HORSE IN A CASE OF CHRONIC POISONING.

No.	Food or organ.	As_2O_3 in parts per million.
1	Grass No. 1	45.00
2	Grass No. 2	107.00
3	Dust from hay	9190.00
4	Ulcer in nose	658.00
5	Contents stomach wet	25.00
6	Contents stomach dried	398.00
7	Urine	59.00
8	Hair of tail	58.00
9	Liver	6.00
10	Thyroid gland	6.00
11	Stomach	4.70
12	Spleen	4.60
13	Pancreas	4.40
14	Small intestines	4.00
15	Brain	3.30
16	Spinal cord	2.60
17	Muscles	2.50
18	Lungs	2.20
19	Bones	2.20
20	Heart	2.10
21	Bladder	1.40
22	Kidney	1.40
23	Right parotid	0.80
24	Fat	0.70
25	Suprarenal	0.06
26	Fluid around heart	0.05
27	Blood	0.03

The horse had fed upon grass and hay containing from twenty to forty-five parts of arsenic trioxide to the million for a period of some months, and for three days had been eating grass containing 107 parts. For several years it had been fed upon grass and hay containing arsenic in varying amounts. Dust shaken from the hay stack in the field where the horses were pastured for three days, contained 9190 parts of arsenic trioxide.

Arsenic in Milk.—Ten samples of milk, most of them mixtures from several cows, were obtained by milking directly into bottles provided with glass stoppers. The analyses gave:

TABLE 6.—ARSENIC IN MILK.

No.	Date, 1906.	Distance from smelter.	No. of cows.	Parts As_2O_3 per million.	Grains to 100 gallons.
1	Sept. 21	4.5 NNE	5	2.94	17.7
2	Nov. 3	3 E	1	0.47	2.83
3	Nov. 3	6 NNE	1	0.70	4.00
4	Nov. 3	4.5 NNE	2	0.18	1.08
5	June 28	4.5 NNE	1	1.40	8.42
6	June 27	5 E	1	1.00	6.02
7	July 2	3 SE	1	4.20	25.28
8	June 28	3 N	5	3.40	20.47
9	June 23	3 W	1	5.70	34.30

The Arsenic Content of Ulcers of the Nose.—A complaint among the horses of smelter regions called the "sore nose" has been observed by the writers in the Anaconda and Salt Lake regions. It is also reported that the same disorder is found in Great Falls, and among the horses of the smelting region in Cornwall. Of the persons who worked on the smelter stacks in determining the arsenic content of the smoke, two became affected with an arsenical rash upon the face, while the nostrils of the third were almost closed by a swelling caused by the irritant action of the flue dust. In the case of horses, one nostril may become closed almost absolutely on account of an ulcer which forms on the lower portion of the nasal partition. Several of these ulcers were taken from the nostrils of different horses and analyzed with the following results:

No.	Distance.	Parts As_2O_3.	No.	Distance.	Parts As_2O_3.
1	2 miles S	254	4	2 miles S	902
2	4.5 miles NNE	587	5	3 miles SW	545
3	3 miles SE	1015			

Undoubtedly the highly arsenical dust from the hay and grass lodges in a fold of the nostril and irritates the mucous membrane until the nose scab is formed. The dust from the hay of the ranch where samples 3 and 5 were obtained, contained 9190 parts of arsenious oxide per million.

In order to see if the cases observed in Salt Lake could be due to this cause, samples were taken in different parts of the district. These samples, taken September 3, 1905, contained from ten to sixty parts of arsenic trioxide to the million, results which would indicate that sufficient arsenic is present to cause the observed effects.[1]

Arsenic in the Hair.—According to the evidence of Mann[2] arsenic is localized in and eliminated by the hair. Large amounts of arsenic were found in the hair of animals of the Anaconda region. The hair of the tail of one horse contained fifty-eight parts of arsenic trioxide to the million, an amount ten times as great as that found in the liver. The hair of a colt contained 605 parts, the liver 4.4 parts, and the bone 13.2 parts, while the

[1] For other results from this district see preceding paper, Table VII.

[2] Report of the Royal Commission, p. 13; and Minutes of Evidence, Vol. 1, p. 139.

grass in the field where the colt was feeding contained only ten parts per million. The hair of a filly pastured five miles north of the smelter gave 460 parts of arsenic. The case is more complicated than those investigated in England, since an unknown fraction of the arsenic in the hair was undoubtedly deposited from the atmosphere. Nevertheless, the results are striking and important.

Normal Arsenic.—Attempts have been made to show that the amounts of arsenic present in the tissues of the animals of smelter regions represent what may be called normal arsenic. This is certainly a perversion of the conclusions of Gautier and Bertrand, for the results obtained by them were of a totally different order of magnitude from those obtained in forensic cases; and they found arsenic only in the thyroid, thymus, brain and skin. Even these results have been criticized by Kunkel,[1] Hödlmoser,[2] Cerny,[3] Stevenson and Mann.[4] The latter writers claim that the arsenic present is wholly adventitious.

No attempt was made by the writers to test Gautier's conclusions, but about forty-five livers from Palo Alto, California, New York City, and Missoula, Montana, were analyzed, using samples of from one hundred to eight hundred grams. Using tests which would detect the presence of 1/1000 mg. of metallic arsenic, in no case was arsenic found. This is sufficient proof that the question of normal arsenic need not come into smelter smoke investigations.

Symptoms.—The following three examples may be taken as typical cases which together exhibit the range of important symptoms which have appeared in connection with arsenical poisoning in the Deer Lodge Valley.

Case (a).—The first example is that of a roan mare owned by a farmer living about eight miles north of the smelter. She was eight years old, weighed thirteen hundred pounds, was sleek and fat, and so far as outward appearances went, perfectly sound. The owner stated in answer to questions, that the animal had fed rarely on pasture but almost entirely on hay, of which she ate much more than the average ration. For nearly a year, however, she had been failing in strength, and was no longer able to do an ordinary day's work, profuse perspiration and total exhaustion following any unusual exertion. An examination showed a "sore nose" scar in one nostril.

The animal was shot and the autopsy made immediately thereafter. The urine was white in color and heavily sedimented; the heart "flabby" and larger than normal; the lungs were covered with a mattery adherent exudate and were "flabby," due to the blocking of the bronchii with a

[1] *Z. physiol. Chem.*, 44, 511–529 (1905).
[2] *Ibid.*, 33, 329-344 (1901).
[3] *Ibid.*, 34, 408 (1901).
[4] Minutes of Evidence, Royal Commission on Arsenical Poisoning.

yellow caseous substance, and the escape of air into the tissues; the liver weighed 17 pounds, 7 pounds above normal; the mucous membrane of the stomach was reddened over certain areas in the fundus; the small intestines showed a great many extensive diffuse red patches; the large intestines were generally badly reddened, and here and there distinctly eroded. An unmistakable odor of garlic was observed when the intestines were opened. The mucous membrane of the uterus and bladder was notably reddened, and the right ovary was gorged with a deep red gelatinous substance. The bone marrow was of a deep yellow color, due to a quantity of yellow oil which filled the interstices and retained its liquid character at ordinary temperatures.

Case (*b*).—The second is a colt, one year old, which was posted two miles south of the smelter on July 3, 1906. It began to appear unthrifty during the fall of the preceding year while on the hill pastures, and at no time thereafter did it show a normal growth. The autopsy showed that this was a case of remote chronic rather than of acute poisoning. The secreting mucous membranes throughout the body were reddened in patches, but only slightly. The hair was shaggy and lusterless, and the whole organism weakened and emaciated.

Case (*c*).—The last case is that of a colt, eleven months old, which had developed normally during the sucking period of six months, when it was weaned and removed to an adjoining pasture early in the month of March. From that time until July 1st it subsisted on hay from a stack in the field. On the date mentioned, following an effort to rope it, the colt had a "fit" and died in convulsions. The stomach showed three distinct, crater-like ulcerations and extensively irritated areas, especially in the folds. The lungs were badly discolored as in necrosis or fatty degeneration. The organ was certainly badly affected, and as soft as a partially decomposed organ. The intestines were highly inflamed, often for five to eight inches in one place, and the whole of the small intestine was covered with inflamed patches.

The first of the cases cited is apparently one in which the arsenic showed its usual stimulating action, strengthening the appetite, promoting the digestion, causing the deposition of much intestinal fat and giving a sleek appearance to the subject. The action was proceeding beyond this stage however, and a breaking down of many of the organs was in evidence. This was a case of progressive chronic poisoning, shown further by the large amounts of arsenic in the bone (20.67 parts per million).

The second case seems to be one of true chronic poisoning which evidently took another course, the stimulating effect being constantly overshadowed by the more destructive action of too large doses. The organism was too weak to recover, even after loss of appetite reduced the ingestion of the toxic agent to a minimum. The stomach was nearly empty, and the liver carried

only very small amounts of arsenic, while the storehouses for arsenic in the organism, the bone and hair, showed excessive amounts. The analytical results were: hair, 605 parts; bone, 13.2 parts; liver, 3.3 parts; and heart, 1.7 parts of arsenic trioxide per million.

The third case is one of recent chronic poisoning, leading rapidly to a culmination in a way truly characteristic of the substance. The liver of this colt contained 31.7 parts, and the kidneys, 2.4 parts of arsenic trioxide per million.

During a considerable time the writers were associated in this work with Dr. D. E. Salmon, of the Bureau of Animal Industry, who very kindly prepared an outline of the more prominent symptoms of the animals as they appeared to him, for use in this publication. These are given as follows:

Symptoms of the Chronic Arsenical Poisoning caused by the Vegetation of Smelter Regions.

Horses.—1, Raised red line at the base of incisor teeth; 2, breath of a garlic odor; 3, loss of spirit, vigor, and endurance; 4, falling of hair; 5, retention of old hair; 6, ulcers of the nose; 7, weakness and imperceptibility of pulse; 8, erosions on the outer side of gums; 9, puffiness above the eye; 10, rough lusterless hair; 11, partial paralysis of hind limbs; 12, with more acute form: (*a*) Difficult breathing, (*b*) labored action of heart, (*c*) dilation of pupils of the eyes, (*d*) partial paralysis of the diaphragm and costal breathing.

Cattle.—1, Shrinkage of milk within a day or two after smoke has been over pastures; 2, salivation and drooling; 3, constipation; 4, rough scurfy coat; 5, eyes red, inflamed, and weeping; 6, loss of appetite; 7, diarrhea when disease becomes more pronounced; 8, tucked up abdomen; 9, loss of flesh; 10, weakness, loss of vigor; 11, cough; 12, breath of garlic odor; 13, droppings covered with mucus; 14, abortion and failure to breed.[1]

In an examination of the animals of a smelter district the chemist may be greatly aided by a careful post-mortem examination, and by the histological study of small specimens taken for this purpose. The most important features to be seen in the sections taken for microscopical investigation are: proliferation of the connective tissue cells, degeneration and desquamation of the tubules in the kidneys, congestion or diapedesis, the occurrence of hemorrhagic areas, and occasionally a total disintegration of the cells. In some cases there is very marked fatty degeneration. The kidneys show these symptoms more prominently than the other organs.

The Anaconda case is of interest not only to the toxicologist, but also to

[1] The diminution in the human birth-rate was noticed during the Manchester epidemic, and the results tabulated by J. Niven. See Royal Commission on Arsenical Poisoning, Minutes of Evidence, Vol. II, Appendix 17, p. 196.

the industrial chemist and the metallurgist, since arsenic in a great number of cases is a constituent of the metallic sulphides, especially those of copper. Large amounts of arsenic are given off by the smelters of Salt Lake, Utah; Everett, Washington; Great Falls, and Butte, Montana; and from many of the smelters of Germany, England, and other countries. In 1854 and 1875, Haubner investigated the smelter smoke disease in the Freiburg district, and various other cases have been studied to a slight extent.

In the decision of Judge Marshall of the Circuit Court of the United States as made November 5, 1906, the conditions existing in the Salt Lake smelter district are described in such a way as to make an interesting comparison with the results of this series of papers. In speaking of the sulphur dioxide he says: "This gas is heavier than air, and when cooled, falls to the ground at a distance from the smelters dependent upon the air currents. When it is brought in contact with moisture, either in the form of rain, freshly irrigated ground, or the moisture present in growing plants and the foliage of trees, sulphurous or sulphuric acid is formed, which is destructive to vegetation. Besides the emission of gas, some flue dust is emitted from the smelters which contains perceptible quantities of arsenic resulting in the death of horses and cows."

In conclusion, the writers wish to thank Dr. John Maxson Stillman for the many suggestions which have been helpful in this work.

THE UNIVERSITY OF MONTANA AND STANFORD UNIVERSITY,
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NOTE ON THE SOLUBILITY PRODUCT.[1]

BY JULIUS STIEGLITZ.

Received April 2, 1908.

Nernst[2] was the first to advance the theory that at a given temperature the solubility of a difficultly soluble electrolyte in water or in aqueous solutions of other electrolytes is dependent on a constant called the solubility product, which is proportional to the concentrations of the ions of the salt, each raised to the power corresponding to the number resulting from one molecule. The constant is an important one in the theory of precipitation and solution and particularly useful in calculations of the solubility of a precipitate in mixtures that are not too concentrated. In Nernst's text-book on physical chemistry,[3] the relation for a difficultly soluble binary salt—such as silver acetate—in water and in solutions containing a salt with a common ion, is developed as follows: calling the total concentrations of the difficultly soluble salt m_0 and m in the saturated water solution and in the salt solution respectively,

[1] Reported at the Chicago meeting of the American Chemical Society.

[2] *Z. physik. Chem.*, 4, 372 (1889).

[3] Translation of the 4th German Edition (1904), p. 527.

and the corresponding degrees of ionization α_0 and α we have first by the application of the isotherm of dissociation, *i. e.*, on the basis of the law of mass action for the two cases:

$$(m_0\alpha_0)^2 = Km_0(l - \alpha_0) \qquad (1)$$

and

$$(m\alpha + x)\, m\alpha = Km\,(1 - \alpha), \qquad (2)$$

in which $(m\alpha + x)$ represents the total concentration of the common ion.

Then, on the basis of the theorem that the undissociated substance has a constant solubility—derived from the law of heterogeneous or physical equilibrium,

$$m_0(1 - \alpha_0) = m\,(1 - \alpha). \qquad (3)$$

Combining the three equations we have

$$(m_0\alpha_0)^2 = m\alpha\,(m\alpha + x),$$

and as $(m_0\alpha_0)^2$, the product of the concentrations of the ions in a saturated, pure aqueous solution at a given temperature, has a definite value, we have in general,

$$m\alpha\,(m\alpha + x) = K_{\text{Solubility product}}. \qquad (4)$$

Substituting the variable symbols C_{Ag}, C_{CH_3COO} and C_{CH_3COOAg}, we can express the first principle for silver acetate by

$$\frac{C_{Ag} \times C_{CH_3COO}}{C_{CH_3COOAg}} = K_{\text{Ionization}}. \qquad (5)$$

and the principle of the constant solubility of the undissociated silver acetate by

$$C_{CH_3COOAg} = k. \qquad (6)$$

Then for the constant solubility product we have simply

$$C_{Ag} \times C_{CH_3COO} = K_{\text{Solubility product}}. \qquad (7)$$

in which C_{Ag} and C_{CH_3COO} represent the concentrations of the silver and acetate ions in any saturated solution of silver acetate, whether in aqueous solution where $C_{Ag} = C_{CH_3COO}$ or in the presence of other salts, where they will usually have different values.

It has long been known, however,[1] that the ionization of strong electrolytes does not conform to the law of mass action—in other words that equations (1) and (2) as used above to develop the theory of the solubility product do not agree with the facts in the cases of such electrolytes, *e. g.*, salts, for which the theory of the solubility product is especially important. The real relation for a salt like silver acetate is that the proportion on the left side of equation (5) grows larger with increasing concentration.[2] This difficulty was recognized by A. A. Noyes,[3] to whom we owe a large part of the

[1] Translation of the 4th German Edition (1904), p. 498.

[2] Rudolphi, *Z. physik. Chem.*, 17, 385 (1895).

[3] *Ibid.*, 6, 241 (1890); 9, 613 (1892); 16, 125 (1895); 26, 152 (1898); 42, 336 (1903)

most exact experimental work on the solubility product, and Noyes attempted to meet the difficulty by assuming that for all solutions in which the concentration of the undissociated substance was kept constant, the product of the ion concentrations is also a constant. Noyes calculated his results on the basis of this assumption and used it even as a method of determining the degrees of ionization of salts in the mixture. Arrhenius[1] showed the error of such an assumption, which cannot be reconciled with his principles of isohydric solution. The latter principle has been established on a safe basis by the work of Arrhenius, Manson, Barmwater, Archibald, McKay, Barnes and others, and has been found to hold, up to a concentration of at least half-normal, for mixtures of salts of the same type as well as for those of different types.[2] We find thus that the application of the law of mass action in equations (1) and (2) to the question of solubility is not justified by experience.

In an important paper published in 1899, Arrhenius[3] took up the investigation of the second fundamental principle involved in the solubility of electrolytes, the widely and generally accepted theory of the constant solubility of the undissociated molecules, as expressed in equations (3) and (6). Originally himself apparently inclined in common with practically all chemists to accept[4] it as a matter of course, as a consequence of the law of heterogeneous or physical equilibrium, but later led to question its correctness, he tested its validity by determining the solubility of silver salts of a number of organic acids in water and in solutions containing an increasing excess of the corresponding sodium salts. Calculating the proportion of ionized and non-ionized silver salt with the aid of the principle of isohydric solutions, he found that as a matter of fact the molecular solubility is not constant but decreases decidedly with the increasing concentration of the total electrolyte.[5] A similar fact has long been known for the relative solubility of gases like carbon dioxide, oxygen, etc., in water and in salt solutions and Arrhenius's result should not have been unexpected.[6]

We thus find that the two fundamental equations on which the theory of the constant solubility product originally was based, are both invalid and we may well ask if this result does not thoroughly discredit and dispose of the theory. Perhaps some such feeling led Arrhenius himself to refrain from calculating the values for the solubility products for the silver salts in his own experiments.

However, if we consider the true relations as now established for the two cases of chemical and physical equilibrium, we have for the

[1] *Z. physik. Chem.*, 11, 391 (1893) and 31, 197 (1899).

[2] A. A. Noyes, Vol. IV, p. 311, *Reports of the Congress of Arts and Science, St. Louis.*

[3] *Z. physik. Chem.*, 31, 197 (1899).

[4] *Ibid.*, 11, 396 (1893).

[5] *Vide* also A. A. Noyes, Reports, etc., Vol. IV, p. 322 (1904).

[6] *Vide* also Nernst, *loc. cit.*, p. 476.

equilibrium between the ions and the undissociated substance of a binary electrolyte a proportion,

$$\frac{C_{Pos.\ ion} \times C_{Neg.\ ion}}{C_{Mol}},$$

which grows *larger* with increase of concentration,[1] and for C_{Mol} the molecular solubility resulting from the equilibrium between the solid phase and the solution, a value growing *smaller* with increasing concentrations of the total electrolyte present.[2] Now it is obvious that with a decreasing value for C_{Mol} and an increasing value for the whole proportion, the ion product, $C_{Pos.\ ion} \times C_{Neg.\ ion}$ possibly might remain constant or approximately constant after all: it is clearly a question for rigorous experiment and calculation to determine whether the ion product does or does not remain constant, that is, whether the values for the proportion and the molecular solubility are inversely porportionate, the proportion growing larger to the same extent as C_{Mol} grows smaller with increased concentrations. Even if it should not prove to be a real, *natural* constant, it might still be found to be sufficiently constant to be of practical value and assistance in the study of the reactions of precipitation and solution.

I have not found in the literature any discussion or investigation of the subject from this point of view; although Arrhenius's paper was published in 1899, even the new edition[3] of Nernst's text-book,[4] as well as other recent editions of books on physical chemistry, such as Jones's "Elements of Physical Chemistry," Mellor's "Chemical Statics and Dynamics,"[5] as well as text-books on the application of physical chemistry to analytical chemistry, do not even refer to it or its extremely important conclusions, but develop the solubility product as given above. I should except a statement made by A. A. Noyes in his address before the Congress of Arts and Science at St. Louis, in which the discrepancy shown to exist by Arrhenius between the principle of isohydric solutions and the old hypotheses concerning solubility is clearly pointed out and the need for further investigation on these lines emphasized.[6]

Considerations[7] of the above nature led me then to complete the calculations of Arrhenius's experimental data on the solubilities of organic silver

[1] Rudolphi, *Loc. cit.*

[2] Arrhenius, *Loc. cit.*

[3] Translation of the 4th German Edition (1904).

[4] P. 595.

[5] 1904, p. 231.

[6] *Loc. cit.*, page 321. Since the presentation of this paper, Professor Noyes has informed me that work along these lines has been continued in his laboratory since 1904.

[7] The theory of the constant solubility product formed an essential element in a chemico-geological investigation carried out by me for Professor Chamberlin (*vide* a forthcoming report, Carnegie Institution), and this study has resulted from that investigation.

salts in the presence of an excess of the corresponding sodium salt, by calculating the value of the ion product in each experiment. To this end, the degrees of ionization of the sodium salts of the fatty acids in the mixtures used had to be calculated first, and this was done with the aid of the principle of isohydric solutions. On account of the form in which Arrhenius's data are presented, the following method was pursued: Arrhenius gives first a table showing the ion concentrations and degrees of ionization of isohydric solutions of silver and sodium acetate. From these data the corresponding total concentrations for the isohydric solutions of the two salts were first calculated and the results expressed in two curves in which the cube roots of the molar concentrations and the degrees of ionization were used as coordinates. The curve obtained for sodium acetate is rectilinear and that for silver nitrate only slightly curved, so the necessary interpolations for the further calculations were easily made. In his other tables, Arrhenius gives the solubility of the silver salts and their degrees of ionization, and the total concentration of the sodium salts, but not the corresponding degrees of ionization. For instance, in the presence of 0.2667 mol. sodium acetate, the solubility of silver acetate is 0.0203 mol., of which 50.4 per cent. is ionized. To find the degree of ionization of the sodium acetate in such a mixture, I found from the curve for the silver salt that an ionization of 50.4 per cent. corresponds to a value of 0.73 for $\sqrt[3]{m}$ and consequently the molar concentration of the silver salt is $(0.73)^3$ or 0.389 when it is considered to be *in its share of the water* according to the isohydric principle. Then its share of the liter of water must be 0.0203/0.389 or 52.2 cc. This leaves 948 cc. for the sodium acetate and its concentration in 948 cc. is 0.2667/0.948 or 0.2813 molar. Then its degree of ionization is 69.6 per cent., according to the curve. The concentration of the acetate ions in each of the isohydric solutions, considered separately, is 0.1961 and 0.1960 for the silver and the sodium acetate, respectively—showing that they were really isohydric. The agreement was not in all cases as close as this, but with one or two exceptions mentioned below, it was satisfactory, the concentrations of the common ion being usually within one per cent. of each other.

In the given case, the total concentration of the acetate ion in the mixture is therefore 0.196, that of the silver ion, as given by Arrhenius is 0.0102 and the value of the ion product in this experiment therefore:

$$C_{Ag} \times C_{CH_3COO} = 0.0102 \times 0.196 \text{ or } 0.00200.$$

All the calculations were made in this way and the following tables give all the results obtained for the acetate, propionate, butyrate, valerate and chloracetate of silver. In the calculations the curves for the acetates were always used to find the degree of ionization for all these salts, following Arrhenius's method.

In the tables the first column gives the molar concentration of the sodium salt used, column 2 its degree of ionization, calculated in the way just described, column 3 the concentration of the ionized part of the sodium salt. Column 4 gives the total solubility of the silver salt, column 5 its degree of ionization, column 6 the concentration of the ionized part of the silver salt and column 7 the concentration of the undissociated part, which represents therefore the molecular solubility of the silver salt. The last column gives the value for the solubility product, $C_{Ag} \times C_{CH_3COO}$. The value for C_{Ag} is found in column 6, and C_{CH_3COO} is the sum of the acetate concentrations given in columns 3 and 6.

TABLE 1.—SILVER ACETATE AT 18.6°.

Na-Acet.	100α.	10^3Acet.	Ag-Acet.	100α′.	10^3Acet.	10^3Mol.	10^5K.
0	..	...	0.0593	72.0	42.7	16.6	182
0.0333	80.0	26.6	0.0474	68.1	32.3	15.1	190
0.0667	78.0	52.0	0.0384	64.4	24.7	13.7	190
0.1333	75.0	100.0	0.0282	58.4	16.4	11.8	191
0.2667	69.6	186.7	0.0203	50.4	10.2	10.1	200
0.5000	63.0	315.0	0.0147	42.8	6.3	8.4	202

TABLE 2.—SILVER PROPIONATE AT 18.2°.

Na-Prop.	100α.	10^3Prop.	Ag-Prop.	100α.	10^3Prop.	10^3Mol.	10^5K.
0	..	..	0.0462	74.5	34.4	11.8	118.4
0.0167	82.0	13.69	0.0393	72.1	28.3	11.0	119.4
0.0333	81.0	27.00	0.0345	69.6	24.0	10.5	122.4
0.0667	78.9	52.63	0.0258	65.5	16.9	8.9	118.0
0.1333	75.3	100.37	0.0191	58.8	11.2	7.9	124.7
0.2667	69.8	186.2	0.0131	50.6	6.6	6.5	127.1
0.5000	63.2	316.0	0.0101	42.9	4.3	5.8	(137.7)

TABLE 3.—SILVER BUTYRATE AT 18.2°.

Na.Butyr.	100α.	10^3Butyr.′	Ag-Butyr.′	100α.	10^3Butyr.′	10^3Mol.	10^5K.
0	..	...	0.0224	81.1	18.2	4.2	33.0
0.0066	86.0	56.8	0.0199	79.6	15.8	4.1	(49.8)
0.0164	84.9	13.9	0.0169	77.3	13.1	3.8	35.4
0.0329	83.0	27.3	0.0131	73.5	9.6	3.5	35.4
0.0658	80.0	52.6	0.0091	67.7	6.2	2.9	36.4
0.1315	75.9	100.0	0.0060	59.9	3.6	2.4	37.3
0.2630	70.1	184.4	0.0040	51.1	2.0	2.0	36.8
0.4930	63.3	312.1	0.0027	43.2	1.2	1.5	37.6

TABLE 4.—SILVER VALERATE AT 18.6°.

Ag-Val.	100α.	10^3Val.′	Ag-Val.	100α.	10^3Val.′	10^3Mol.	10^5K.
0	..	...	0.0095	87.3	8.3	1.2	6.9
0.0175	86.5	15.1	0.0047	81.1	3.8	0.9	7.2
0.0349	84.0	29.3	0.0030	75.5	2.2	0.8	6.9
0.0689	80.1	55.9	0.0018	68.1	1.2	0.6	6.9
0.1395	75.8	105.7	0.0015	59.7	0.9	0.6	(9.6)

TABLE 5.—SILVER CHLORO-ACETATE AT 16.9°.

Na-ClAcet.	100α.	10^3ClAcet.′	Ag-ClAcet.	100α.	10^3ClAcet.′	10^3Mol.	10^5K.
0	..	..	0.0644	71.1	45.8	18.6	209.8
0.0333	79.8	26.6	0.0499	67.6	33.7	16.2	202.2
0.0667	78.1	52.1	0.0405	63.9	25.9	14.6	203.3
0.1333	74.8	99.71	0.0299	58.1	17.4	12.5	202.3
0.2667	69.4	185.1	0.0208	50.4	10.5	10.3	205.8
0.5000	63.2	316.0	0.0162	42.8	6.9	9.3	222.0

The experimental results of Nernst's determinations of the solubility of silver acetate in the presence of sodium acetate and silver nitrate, respectively, were also recalculated. Nernst used the isohydric principle in determining the degrees of ionization of the salts in the mixtures, but considered the salts to ionize with about equal readiness. Such is not the case, if we accept Arrhenius's determinations of the ionization of silver acetate, the values for which, it is true, were very largely obtained by extrapolation. But these same values having been used in bringing the proof that the molecular solubility decreases with the increasing concentrations of the total electrolyte, it seems most reasonable to use the values also for the determinations of the solubility product of the same salt. In Tables 6 and 7 the results of the recalculation of Nernst's data are tabulated, the degrees of ionization being determined by the application of the isohydric principle in the usual way—the two salts present being supposed to divide the water in such a way as to give solutions containing the same concentration of the common ion. The division of the water was rapidly ascertained by trial calculations with the help of the curves of dissociation for the third root of the concentrations. The columns in these tables have in part a different significance from the columns of the previous tables: column 1 gives the molar concentration of the sodium acetate (silver nitrate in Table 7) used in excess, column 2 gives the portion of the water, in cubic centimeters, in which all the sodium acetate (silver nitrate) is supposed to be dissolved to form a solution isohydric with the solution of silver acetate in the rest of the water. Column 3 gives the degree of ionization of the sodium acetate (silver nitrate), column 4 the concentration of the common ion in this solution, 5 the total concentration of silver acetate, 6 its degree of ionization, and column 7 the concentration of the common ion in the isohydric silver acetate solution. The last column gives the values for the solubility product.

TABLE 6.—SILVER ACETATE AT 16°.

Na-Acet.	cc. H_2O.	100α.	10^3Acet.′	Ag-Acet.	100α.′	10^3Acet.′	10^5K.
0	...	....	.....	0.0603	70.8	0.0427	182.3
0.061	656	78.6	0.0731	0.0392	64.5	0.0735	185.4
0.119	843	75.8	0.1070	0.0280	59.7	0.1065	178.5
0.239	937	70.8	0.1738	0.0208	52.3	0.1727	188.2

TABLE 7.—SILVER ACETATE AT 16°.

$AgNO_3$.	cc. H_2O.	100α.	$10^3Ag.'$	Ag-Acet.	100α.'	$10^3Ag.'$	10^5K.
0	...	....	.....	0.0603	70.8	0.0427	182.3
0.061	650	82.0	0.0770	0.0417	64.0	0.0763	204.4
0.119	825	78.4	0.1131	0.0341	58.6	0.1142	227.2
0.230	944	74.0	0.1803	0.0195	51.7	0.1809	182.1

Considering the data in the last columns of the tables, we find that the value of the solubility product increases at most from five to ten per cent. in mixtures down to a concentration of half-molar,[1] and in some of the experiments (Tables 4, 5, 6 and 7), it shows practically no variation of moment. All the variations may well be within the limit of errors of experiment and computation in an investigation in which a large part of the calculations are based on an extrapolated curve. Of the serious discrepancies, the bracketed value in Table 3 (line 2) corresponds to an experiment, the figures of which given by Arrhenius show, by the method of calculation used above, a decided divergence from the principle of isohydric solutions—so there must be an error of observation or record in it. The bracketed value in Table 4, last line, also corresponds to an experiment in which there is probably some error, as is indicated by a consideration of the values in the next to the last column of the table.

We find thus empirically that in the case of the silver salts of these organic acids the principle of the constant solubility product, faulty as its original theoretical basis was, is sufficiently in agreement with the observed facts to prove of some practical value. This conclusion confirms the results of the experimental data of others on the solubility of a salt in the presence of other electrolytes having a common ion. Nernst's results have already been mentioned. Findlay's[2] experiments on the relative solubility of lead iodide and sulphate, although the theoretical development is open to the same criticism made above, were nevertheless calculated correctly according to the isohydric principle and they agree with the theory of a constant solubility product. In this case, the condition of the equilibrium in the mixtures was determined not only on the basis of conductivities but also by measurements of electromotive forces. Bodländer's[3] work on the solubility of calcium carbonate in water containing carbon dioxide in equilibrium with varying partial pressures of carbon dioxide

[1] A. A. Noyes, *loc. cit.*, p. 322, pointed out that in the case of a solution saturated simultaneously with thallous chloride and bromate, the product of the ion concentrations of each is increased by about five per cent. Each salt gives an approximately $^1/_{40}$ molar solution. This case was considered *typical*.

[2] *Z. physik. Chem.*, 34, 409 (1900).

[3] *Ibid.*, 35, 23 (1900). *Vide* also a paper by Stieglitz to be published in the report of the Carnegie Institute of Washington, in which the data presented by Bodländer are recalculated on the basis of more recent determinations of the constants involved.

led to excellent constants: the theoretical treatment started from the assumption of a constant solubility product for calcium carbonate. In the address referred to, A. A. Noyes[1] mentions two or three other cases, such as the solubility of lead iodide in the presence of potassium iodide and of lead chloride in the presence of potassium chloride, and of calcium hydroxide in the presence of ammonium chloride, in which cases the theory is said to be sustained approximately.

In view of these facts and also in view of the results of the complete calculation of Arrhenius's data on the solubility of the silver salts, which removed the last *theoretical* foundation for the solubility product constant, we may well consider it for the present to be an approximate empirical principle, much in the same way as so many other important principles concerning electrolytes are still simply empirical, such as the isohydric principle itself, and the various rules—Rudolphi's, van't Hoff's, Kohlrausch's—expressing the equilibrium between strong electrolytes and their ions. A great deal more exact work on the extent of the reliability of the solubility principle will obviously be necessary to determine what the true relations are. If it should be confirmed still further and firmly established, the question of its theoretical bearing will become an interesting one—particularly in its relation to the other empirical principles of solutions of electrolytes.

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[CONTRIBUTION FROM THE LABORATORY OF BIOLOGICAL CHEMISTRY OF THE HARVARD MEDICAL SCHOOL.]

A DIAGRAMMATIC REPRESENTATION OF EQUILIBRIA BETWEEN ACIDS AND BASES IN SOLUTION.

BY LAWRENCE J. HENDERSON.

Received March 27, 1908.

During a series of investigations concerning the adjustment of neutrality in the animal organism,[2] it has been found convenient to construct diagrams representing the equilibria between bases and acids of different ionization constants in solution of varying acidity and alkalinity. These diagrams, simple consequences of the concentration law, and of the principle of isohydric solutions, seem to possess certain advantages over other methods of presentation of the somewhat involved conditions. Especially are they useful to indicate immediately the adjustment of all possible equilibria of this sort, with at least a moderate degree of accuracy, and on account of such practical usefulness they are here presented.

[1] *Loc. cit.*, p. 322.

[2] For general conclusions and the literature see Henderson, *American Journal of Physiology*, May, 1908.

Let it be required to find the extent to which any acid, HA, of any ionization constant, k, present in aqueous solution together with a varying amount of its salt of a strong base, for instance sodium hydroxide, exists uncombined as free acid in the solution, when the hydrogen ion concentration is equal to (H^+).

The ionization of the acid may be expressed by the reaction,

$$HA = H^+ + A^-$$

whence

$$(H^+) = k\frac{(HA)}{(A^-)}.$$

For all weak acids the concentration of undissociated molecules (HA), is almost precisely equal to the total concentration of free acid, and the concentration of the anions, (A^-), is equal to the total quantity of salt, NaA, multiplied by its degree of ionization, γ. Thus one obtains the equation

$$(H^+) = \frac{k}{\gamma} \times \frac{HA}{NaA}.$$

Let

$$\frac{k}{\gamma} = C$$

then

$$(H^+) = C \times \frac{HA}{NaA}. \qquad (1)$$

In this equation C is always greater than k. Under ordinary circumstances its value may be stated as follows:

$$2k > C > k.$$

In any particular case it is an easy matter to estimate the value of C, but for ordinary purposes very little error is involved in assuming equality between C and k, especially in very dilute solutions. The effect of concentration, however, is usually quite small.

From equation 1, there may be calculated the values of the ratio $\frac{HA}{NaA}$ corresponding to any values of (H^+) and C, and from the numbers thus obtained, the per cent. of free acid, $\frac{HA}{HA + NaA}$, may be deduced. On the accompanying diagram the results of such calculation are indicated.

Values of C are plotted logarithmically as abscissas; per cents. of acid uncombined, $\frac{HA}{HA+NaA}$, are plotted as ordinates The several curves are drawn to connect points corresponding to equal hydrogen-ion concentrations, that is to say, to equal degrees of acidity and alkalinity, and these concentrations are indicated on the curves.

The use of the diagram may be illustrated as follows for the case of car-

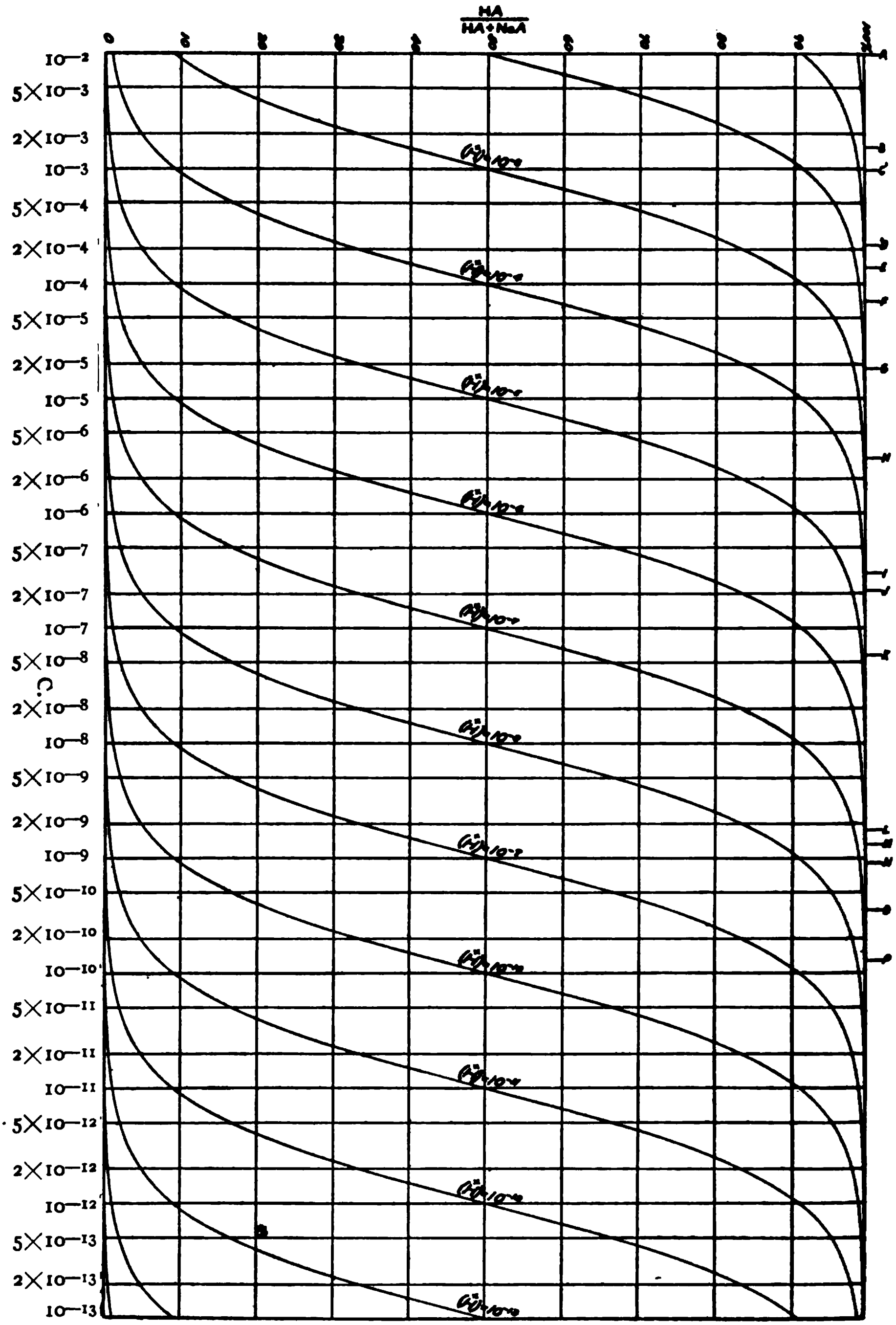
HA / HA+NaA
10⁻²
5×10⁻³
2×10⁻³
10⁻³
5×10⁻⁴
2×10⁻⁴
10⁻⁴
5×10⁻⁵
2×10⁻⁵
10⁻⁵
5×10⁻⁶
2×10⁻⁶
10⁻⁶
5×10⁻⁷
2×10⁻⁷
10⁻⁷
5×10⁻⁸
2×10⁻⁸
10⁻⁸
5×10⁻⁹
2×10⁻⁹
10⁻⁹
5×10⁻¹⁰
2×10⁻¹⁰
10⁻¹⁰
5×10⁻¹¹
2×10⁻¹¹
10⁻¹¹
5×10⁻¹²
2×10⁻¹²
10⁻¹²
5×10⁻¹³
2×10⁻¹³
10⁻¹³

Fig. 1.

bonic acid. The ionization constant of carbonic acid[1] is very nearly 3×10^{-7}. In a decinormal solution of sodium bicarbonate the degree of ionization is approximately 0.8. These numbers yield the equation

$$C = \frac{3.0 \times 10^{-7}}{0.8} = 3.8 \times 10^{-7}.$$

On examination it appears that the abiscissa corresponding to $C = 3.8 \times 10^{-7}$ is cut

At the ordinate. Per cent.	By the curve of hydrogen-ion concentration.
0.3	10^{-9}
2.7	10^{-8}
20.7	10^{-7}
72.3	10^{-6}
96.3	10^{-5}
99.6	10^{-4}

That is to say, at a hydrogen ion concentration 1×10^{-9} *N*, 0.3 per cent. of all the carbonic acid must be present as free acid, and as acidity increases this fraction increases, as defined by the above table, until when the acidity is greater than 1×10^{-4} *N* hydrogen-ion concentration nearly all the carbonic acid must be free.

Disregarding the incompleteness of ionization, the following table is obtained from the diagram ($C = 3.0 \times 10^{-7}$).

Ordinate. Per cent.	Curve of hydrogen-ion concentration.
0.4	10^{-9}
3.2	10^{-8}
25.0	10^{-7}
77.0	10^{-6}
97.0	10^{-5}
99.6	10^{-4}

Evidently the differences between this table and the former one are unimportant for approximate estimations.

On the diagram, the letters above the lines of abscissas designate the ionization constant of these acids as follows:

Letter.	Acid.	*k*.	Letter.	Acid.	*k*.
A	Maleic[2]	1.17×10^{-2}	I	Carbonic[3]	3.04×10^{-7}
B	Monochloracetic[2]	1.55×10^{-3}	J	NaH_2PO_4[5]	2.0×10^{-7}
C[1]	Tartaric[2]	9.7×10^{-4}	K	Hydrogen sulphide[3]	5.7×10^{-8}
D	Formic[2]	2.14×10^{-4}	L	Boric[3]	1.7×10^{-9}
E	Lactic[2]	1.38×10^{-4}	M	Hydrocyanic[3]	1.3×10^{-9}
F	Aspartic[4]	6.9×10^{-5}	N	Alanine[4]	9.0×10^{-10}
G	Acetic[2]	1.80×10^{-5}	O	Glycocoll[4]	3.4×10^{-10}
H	Picolinic[2]	3.0×10^{-6}	P	Phenol[3]	1.3×10^{-10}

[1] Walker and Cormack, *J. Chem. Soc.*, **77**, 20 (1900).
[2] Ostwald, *Z. physik. Chem.*, **3**, 418 (1889).
[3] Walker and Cormack, *J. Chem. Soc.* **77**, 20 (1900).
[4] Winkelblech, *Z. physik. Chem.*, **36**, 587 (1901).
[5] Private communication of Professor A. A. Noyes.

For convenience the ionization constants of certain acid substances are indicated as values of C on the diagram. In like manner, equilibria of these acids, and of all other acid substances, except very strong acids, whose case is obviously a special one, are defined by the diagram and may be read off from it directly, correcting for the ionization of the salt, if necessary.

By a somewhat different use of the diagram, equilibria in complicated mixtures are defined, and also isohydric solutions made up of any acids (with the exception noted) and strong bases.

In a solution made by neutralizing sodium hydroxide with phenol, boric acid, hydrogen sulphide, carbonic acid, picolinic acid, and acetic acid, let it be required to find the extent to which the base is combined with the several acids, the hydrogen ion concentration being 1×10^{-7}.

The curve of hydrogen ion concentration 1×10^{-7} cuts the abscissas

	Of	At the ordinate of per cent.
P	Phenol	99.9
L	Boric acid	98.5
K	Hydrogen sulphide	64.5
I	Carbonic acid	25.0
H	Picolinic acid	3.5
G	Acetic acid	0.4

Accordingly, in this solution, phenol is hardly at all combined with sodium, and acetic acid is almost completely combined with it. The other acids are partly free, approximately in the degrees indicated by the above percentages. The above numbers serve also to define one series of isohydric solutions made up of these acids and their sodium salts.

In like manner, all possible similar mixtures and all possible similar isohydric solutions are defined by the diagram.

The case of bases of varying strengths in equilibrium with strong acids, is strictly analogous. For the ionization reaction of a base

$$BOH = B^{+} + OH^{-}.$$

The following equation may be derived:

$$(OH^{-}) = C \times \frac{BOH}{BCl}.$$

This equation yields the diagram represented in Fig. 2, in form identical with the diagram of Fig. 1. The curves, however, represent hydroxyl ion concentrations; the abscissas are as before, values of C plotted logarithmically, and ordinates indicate per cent. of base which is uncombined with acid. The diagram is to be used in precisely the same way as Fig. 1, and for convenience the values of *k* for certain bases are indicated approximately upon it as values of C.

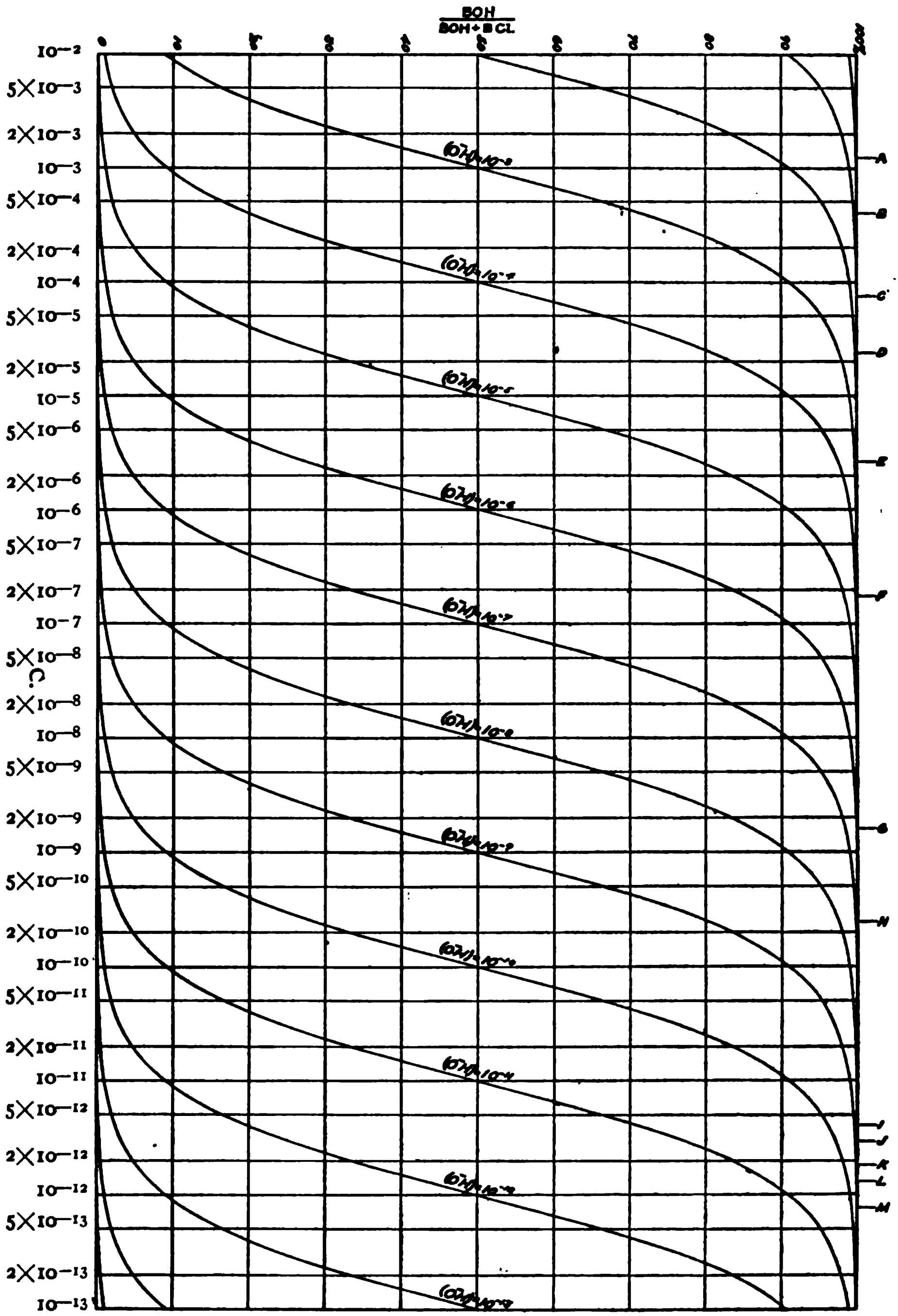
BOH / BOH + BCL
10⁻²
5×10⁻³
2×10⁻³
10⁻³
5×10⁻⁴
2×10⁻⁴
10⁻⁴
5×10⁻⁵
2×10⁻⁵
10⁻⁵
5×10⁻⁶
2×10⁻⁶
10⁻⁶
5×10⁻⁷
2×10⁻⁷
10⁻⁷
5×10⁻⁸
2×10⁻⁸
10⁻⁸
5×10⁻⁹
2×10⁻⁹
10⁻⁹
5×10⁻¹⁰
2×10⁻¹⁰
10⁻¹⁰
5×10⁻¹¹
2×10⁻¹¹
10⁻¹¹
5×10⁻¹²
2×10⁻¹²
10⁻¹²
5×10⁻¹³
2×10⁻¹³
10⁻¹³
A
B
C
D
E
F
G
H
J
K
L
M

Fig. 2.

These bases and their ionization constants are as follows:

Letter.	Base.	k.
A	Diethylamine[1]	1.26×10^{-3}
B	Methylamine[1]	5.0×10^{-4}
C[1]	Trimethylamine[1]	7.4×10^{-5}
D	Ammonia[1]	2.3×10^{-5}
E	Hydrazine[1]	2.7×10^{-6}
F	$(CH_3)_3SnOH$[1]	1.7×10^{-7}
G	*p*-Toluidine[2]	1.6×10^{-9}
H	Aniline[2]	4.9×10^{-10}
I	Alanine[3]	3.8×10^{-12}
J	Glycocoll[3]	2.9×10^{-12}
K	Sarcosine[3]	1.8×10^{-12}
L	Aspartic acid[3]	1.3×10^{-12}
M	Betaine[3]	7.6×10^{-13}

Summary.

A diagram is presented which expresses the requirements of the concentration law regarding the equilibrium in solution between strong bases and acids of all strengths. A precisely similar diagram indicates the equilibrium in solution between strong acids and bases of all strengths. (The diagrams are not useful for solutions containing both strong bases and strong acids in which the acidity or alkalinity is high.)

These diagrams define with considerable accuracy the conditions of equilibrium at all hydrogen- and hydroxyl-ion concentrations, between all bases and all acids with the above-mentioned exceptions, and in all mixtures of such substances. They also define all isohydric solutions of such substances in which this quality is dependent upon equality in concentration of hydrogen- and hydroxyl-ions alone.

THE HEATS OF SOLUTION OF THE THREE FORMS OF MILK-SUGAR.

By C. S. Hudson and F. C. Brown.

Received April 15, 1908.

Milk-sugar can be crystallized from solution in two forms, one of which is a monohydrate, $C_{12}H_{22}O_{11}.H_2O$, and the other an anhydrous modification, $C_{12}H_{22}O_{11}$, named β-anhydrous milk-sugar. When either of these crystalline milk-sugars is dissolved in water it changes partially to the other form until a condition of dynamic equilibrium is reached in which both forms are present in the solution. In distinction from the β-anhydride of milk-sugar there is an α-anhydride which is produced when hydrated milk-sugar is heated at 125° to constant weight. This α-anhy-

[1] Bredig, *Z. physik. Chem.*, 13, 289 (1894).

[2] Nernst, Theoretische Chemie, 3rd Edition, p. 497.

[3] Winkelblech, *loc. cit.*

dride is markedly hygroscopic, it dissolves in water with an evolution of considerable heat, and its freshly prepared solutions are identical with those of hydrated milk-sugar; these facts indicate that the α-anhydride is unstable in the presence of water and changes immediately to hydrated milk-sugar when dissolved. Measurements of the rate at which the equilibrium between the hydrate and the β-anhydride is approached and of the proportions of the two forms that are finally present in the solution have already been published.[1] The present research is a study of the heats of solution of these three forms of milk-sugar under the guiding hypothesis that when any one of them is dissolved in water there occurs the incomplete or balanced reaction in solution between the hydrate and the β-anhydride. These heats of solution are not simple quantities, because the dissolving of any form of the sugar is usually complicated by the presence of a second heat effect due to the change to the stable mixture of hydrate and β-anhydride. In order to distinguish the component parts of these complex heat effects the following nomenclature is adopted:

The *initial heat of solution* is the heat that is produced when any form of the sugar is dissolved under such conditions that the subsequent change to the stable mixture of hydrate and β-anhydride is greatly retarded.

The *final heat of solution* is the total heat that is produced when any form of the sugar dissolves to give a solution in which the stable mixture is present.

The *heat of passage* of one form to the other is the heat that is produced when a given quantity of the one form changes in solution to an equivalent quantity of the other form.

To illustrate these definitions by an example, when hydrated milk-sugar dissolves in cold water quickly no appreciable amount of the β-anhydrous form is produced and the heat which is absorbed during the dissolving is the initial heat of solution of the hydrate. On the other hand, if the hydrated sugar dissolves in alkaline water its partial change to the β-anhydrous form is instantaneous and the heat absorbed in dissolving is in this case the final heat of solution, which is obviously the sum of the initial heat of solution of the hydrate and the heat of passage of that portion of the hydrate which subsequently changes to the β-anhydride.

The Method of Measuring the Heats of Solution.—The calorimeter that was used is similar to one that has been described by A. A. Noyes.[2] The inner can is of brass, silver-plated and polished, and of a liter capacity. It rests upon three corks in a polished tin vessel and this in turn is supported by corks within the outermost vessel which is double-walled and water-jacketed. A close covering of thick felt completely surrounds the

[1] THIS JOURNAL, **26**, 1065–1082 (1904).

[2] *Z. physik. Chem.*, **43**, 513–38 (1903).

calorimeter. The temperatures were read from a certified Beckmann thermometer graduated to hundredths of a degree. The contents of the inner can were stirred by a silver-plated brass propeller driven by an electric motor. In most of the experiments on the heats of solution the finely powdered sugar was loosely packed in a silver-plated brass tube of 50 cc. capacity which was suspended from the cover of the inner can. An aluminum disk was cemented water-tight in the lower end of this tube with paraffin and could be punched out at the proper time with a glass rod inserted through the calorimeter coverings. This arrangement allowed a sudden and controllable mixing of the dry sugar with the water while the calorimeter remained closed.

The Initial Heat of Solution of Hydrated Milk-Sugar.—Pure hydrated milk-sugar was prepared by recrystallizing once a very good quality of commercial milk-sugar crystals, and it was dried to constant weight at 100°. This hydrate does not lose its water of crystallization at this temperature even under prolonged heating. The determination of its initial heat of solution was carried out at 20° by the method that has just been described and the resulting data are given in the following table. In order to make certain that all the sugar dissolved, the stirrer was stopped and the calorimeter opened immediately after several of the measurements, but in no case could any undissolved sugar be seen.

TABLE I.—INITIAL HEAT OF SOLUTION OF HYDRATED MILK-SUGAR AT 20°.

Mass of water. Grams.	Mass of sugar.	Total water equivalent.[1]	Temperature change.	Heat of solution.	Time to dissolve. Minutes.[2]
999	31.26	1038	—0.361	—12.0	4
984	26.13	1022	—0.304	—12.0	2
999	26.10	1037	—0.302	—12.0	3
991	26.23	1029	—0.306	—12.0	2
996	26.08	1034	—0.302	—12.0	1
993	25.87	1031	—0.296	—11.8	2
987	25.87	1025	—0.302	—12.0	2
998	11.23	1031	—0.128	—11.8	1
1003	29.60	1042	—0.343	—12.1	2
1000	37.07	1041	—0.400	—11.8	4
			Average	—12.0	

The average of these ten determinations is —12.0 gram calories per gram for the initial heat of solution of hydrated milk-sugar at 20°. This value is somewhat larger than those which others have found, Berthelot[3]

[1] The water equivalent of the inner calorimeter and its attachments, including the immersed portion of the thermometer was calculated to be 29.9 grams. The specific heat of milk-sugar is 0.30, Magie, *Physical Review*, 16, 381 (1903).

[2] The sugar was assumed to be completely dissolved when the rate of change of the temperature reached the value that it had before the sugar was added.

[3] *Méchanique Chimique*, I, 545.

gives —10.2, Brown and Pickering[1] —11.5, Magie[2] —11.5. These differences are probably principally due to the fact that hydrated milk-sugar has a large temperature coefficient of its heat of solution. Magie has found the molecular heat of hydrated milk-sugar to be 108 in the solid state and 165 in solution, therefore the heat absorbed by the solution of 1 gram must increase (165–108)/360 = 0.16 calorie for each degree rise of temperature. According to this, the difference between the value here found for the heat of solution and that given by Brown and Pickering and by Magie can be explained by a difference of only 3° in the temperature of the experiments. As Brown and Pickering's measurement was made at 16°, and probably also Magie's, while the present ones were performed at 20°, it is evident that an excellent agreement has been obtained by the different observers. Solubility measurements on hydrated milk-sugar also show that the heat of solution increases with the temperature, for if the solubilities at 15° and 25° are used to calculate the heat of solution for this range by the well-known method of van't Hoff, —11.5 calories is obtained,[3] but if those at 0° and 15° are employed —10.3 is found. If the former value is considered to refer to 20° and the latter to 7.5° the change in the heat of solution per degree is 0.10 calorie which agrees with the coefficient that was found above from the molecular heats.

In the data given in Table 1 there is no indication that the heat of solution changes in value according as the sugar is dissolved in much water or in little. If such an effect were present the solutions would of necessity also show considerable heat of dilution; this fact was accordingly made use of as a direct test. Fifty cc. of a semi-normal solution of milk-sugar were put in the tube of the calorimeter and after constant temperature was attained the bottom of this tube was punched out and the solution allowed to mix with 800 cc. water, which was 9 grams of sugar passing from half to three hundredths molal concentration. In the two experiments rises of temperature of 0.001° and 0.003° were observed, and they are so small that the absence of any considerable heat of dilution can be considered established. It follows from this that the heat of solution of milk-sugar does not change with the concentration in dilute solution (*e. g.*, below 0.3 molal) and changes only very slightly in concentrated solutions.

As has been mentioned, hydrated milk-sugar forms β-anhydrous milk-sugar slowly during many hours after its solution in cold water. In order to make certain that the data given in Table 1 refer to the *initial* heat of solution it must be shown that this chemical change in the solution did not proceed far enough during the time of the measurement to give

[1] *J. Chem. Soc.*, **71**, 783 (1897).
[2] *Phys. Rev.*, **16**, 381 (1903).
[3] See page 970 below.

any heat effect. Now in that experiment which required the longest time, four minutes, 3 per cent. of the dissolved hydrate changed to the β-anhydride, according to previous measurements of the rate of this change.[1] It will be shown later in this article that when the change proceeds to equilibrium the heat effect is small, certainly not greater than one calorie per gram of sugar transformed; therefore only three hundredths of a calorie at the most is the error that is due to the change of the hydrated sugar after dissolving, and it can be neglected.

The Preparation of Pure β-Anhydrous Milk-Sugar.—Three methods for preparing β-anhydrous milk-sugar have been published; in the first a solution of any form of milk-sugar is boiled to dryness,[2] in the second alcohol and ether are added to a hot solution to precipitate the anhydride,[3] while in the third the solution is allowed to crystallize slowly at 95° from supersaturation.[4] The first and second of these methods give an impure anhydride contaminated with varying amounts of hydrated milk-sugar, but by following the directions given below which are based upon the third method, it has been found possible to secure a good yield of the β-anhydride in large crystals which are colorless and free from hydrate.

Commercial crystallized milk-sugar is dissolved in hot water to form a saturated solution at 100°, which is then decanted into a copper beaker and rapidly boiled until its boiling-point rises to 104–105°. The copper beaker is then suspended in boiling water or steam for twenty-four hours. A crust forms over the solution soon after boiling ceases which hinders further evaporation and at the end of the twenty-four hours numerous well-formed crystals are found hanging to the sides of the beaker and the crust. The bottom of the beaker is covered with a compact mass of minute crystals which are rejected, as it is impossible to free them from the mother-liquor. It is well to roughen the surface of the copper beaker in order that the crystals may adhere better. To free the crystals from the solution, which is a thick syrup, an opening is cut through the crust, the beaker removed from the heater and as much as possible of the hot solution poured off; the crystals are then removed from the beaker, pressed between filter papers and immediately washed by decantation with glycerol heated to 140°, followed by hot 95 per cent. alcohol and then by ether.

In order to test the crystals that were prepared by this method for the presence of traces of the hydrate, a finally saturated solution of hydrated milk-sugar was prepared at 20°, filtered to free it of all suspended particles,

[1] THIS JOURNAL, 26, 1076 (1904).
[2] Erdman, *Ber.*, 13, 1915–31 (1880).
[3] Tanret, *Bull. soc. chim.* [3], 15, 354 (1896).
[4] Hudson, *Z. physik. Chem.*, 44, 488 (1903).

and cooled to 0°, at which temperature such a solution is known to be supersaturated with respect to the hydrate but greatly undersaturated with respect to the anhydride.[1] Several crystals of the anhydride that were prepared as described above were then placed in this solution. They dissolved completely without leaving a visible trace of insoluble matter, which would not have been the case if the crystals contained particles of the hydrate. This method of testing for the presence of the hydrate is quite delicate and the result shows conclusively that the β-anhydride is pure. This test for purity can be applied to a few other substances for which such a test has heretofore been lacking, for example to the β-anhydrous forms of glucose, galactose and the other mutarotating sugars.

The specific gravity of pure β-anhydrous milk-sugar at 20° is 1.59, of the hydrated form 1.54.

The Initial Heat of Solution of β-Anhydrous Milk-Sugar.—The initial heat of solution of this form of the sugar was measured in the same manner that has been described in the case of the hydrate. The sugar sample marked one was a year old, the other two were freshly prepared. The results are given in Table 2.

TABLE 2.—INITIAL HEAT OF SOLUTION OF β-ANHYDROUS MILK-SUGAR AT 20°.

Mass of water. Grams.	Mass of sugar.	Total water equivalent.	Temperature change.	Time to dissolve. Minutes.	Sample number.	Heat of solution.
716	13.7	749	—0.039	2	1	—2.1
902	29.6	939	—0.063	2	1	—2.0
736	15.4	768	—0.051	2	2	—2.5
464	8.1	497	—0.038	1	3	—2.3
686	13.1	710	—0.051	3	3	—2.3

These experiments give —2.3 calories per gram as the heat of solution and since the chemical change that occurs in these solutions is the reverse of that in the solutions of the hydrate it proceeds too slowly to affect the measurements, and the value obtained is the initial heat of solution. The values for the heat of solution of this anhydride that have been found by previous observers are all larger than the above, undoubtedly because some hydrate was present in their samples; Brown and Pickering[2] found —5.4, Magie and Hudson[3] —3.6.

A Precipitated Milk-Sugar Showing No Mutarotation.—If a solution of any form of milk-sugar is kept for a day at room temperature or boiled and cooled, to allow the reversible chemical change that occurs in such

[1] THIS JOURNAL, 26, 1071–1074 (1904). The concentration of β-anhydride in a saturated solution of the hydrate at 20° is only about one-quarter the initial solubility of the anhydride at 0°.

[2] *J. Chem. Soc.*, 71, 783 (1897).

[3] *Princeton Univ. Bull.*, April, 1902.

solutions to reach equilibrium, and a mixture of strong alcohol and ether is then added, a crystalline precipitate is formed which does not show mutarotation when it is dissolved in water as do the other forms of milk-sugar. Tanret[1] who discovered this precipitate in 1896 regarded it until recently as a new form of milk-sugar, the stable modification to which the other forms revert in solution, ascribed to it the formula $C_{12}H_{22}O_{11}.\frac{1}{2}H_2O$, and named it β-lactose. It is now generally accepted that this form is a mechanical mixture of hydrated and β-anhydrous milk-sugar in about the proportions in which they are present in solution in equilibrium. The view that this form of milk-sugar is such a mixture was expressed six years ago[2] and direct evidence was given to support it; but as the publication in which this evidence appeared had small circulation the data are presented again, using, however, the more accurate values of the heat of solution that are now at hand. If the alcoholic precipitate is a mixture of hydrated and β-anhydrous milk-sugar its initial heat of solution will be intermediate between those of its constituents. The exact value can be calculated from the fact that the two forms must be present in the mixture in the same proportion in which they occur in the stable solution or otherwise the precipitate would show mutarotation when dissolved. It has been shown from solubility measurements[3] that this proportion at room temperature is 1.5 parts β-anhydride to each part hydrate; the initial heat of solution of such a mixture is therefore calculated to be $-[12.0 + (2.4)(1.5)] \div 2.5 = -6.2$ calories. Magie and Hudson[1] found by experiment the value -6.5 calories for Tanret's alcoholic precipitate. The agreement of these values is clear evidence that this precipitate is a mechanical mixture of hydrated and β-anhydrous milk-sugar.

The Heat of Passage in Solution between the Forms of Milk-Sugar.—The establishment of equilibrium between the two forms of milk-sugar in solution proceeds so slowly at room temperature that no noticeable heat effect due to the transformation ordinarily occurs. Although the rate of production of heat in these solutions under usual conditions is thus too slow to admit of its measurement, the velocity of the chemical change can be enormously accelerated by suitable catalytic agents, especially an alkali, and the heat is then produced very quickly and can be measured.[4]

In the following experiments milk-sugar hydrate was dissolved quickly in water at 20° and immediately after its complete solution a small quantity, usually 0.5 cc., of tetranormal sodium hydroxide was added

[1] *Loc. cit.*

[2] *Princeton Univ. Bull.*, April, 1902.

[3] THIS JOURNAL, 26, 1074 (1904).

[4] This is the method that was used by Brown and Pickering (*loc. cit.*) in measuring several such heat effects in the carbohydrate group.

and the immediate rise in temperature measured. An equal quantity of the alkali was then again added and the accompanying rise in temperature again noted. The difference between the first rise and the second is taken to be due to the partial change of the hydrated milk-sugar to the β-anhydride. This conclusion is not strictly correct, and if theory were exactly adhered to the addition of the alkali that was made to the already alkaline solution should have been made to a neutral solution of milk-sugar which had reached equilibrium by long standing, but as several experiments showed that the two methods of addition of the alkali gave the same heating effect the more convenient one was subsequently followed. To make certain that the first addition of alkali caused a sufficiently rapid attainment of equilibrium, the change of rotation of several solutions was observed in the polariscope immediately after 0.5 cc. of alkali was added; the rotation was not quite constant at the end of one minute but did not change at all after two, proving that the catalysis was sufficiently rapid. As from five to twenty minutes elapsed in the experiments given below between the dissolving of the hydrate and the first addition of the alkali it is necessary to correct for the amount of hydrate that was transformed to β-anhydride during this interval; this quantity was calculated from the previous measurements of the velocity of the reaction at 20° and it is recorded in column five. The values in column four are calculated from the equilibrium constant of the reaction, 40 per cent. of the sugar in stable solutions being hydrate and 60 per cent. β-anhydride at 20°.

TABLE 3.—HEAT OF PASSAGE IN SOLUTION OF HYDRATED MILK-SUGAR TO β-ANHYDRIDE AT 20°.

Water. Grams.	Total water equivalent.	Mass of hydrate originally dissolved.	Mass of hydrate finally changed.	Mass of hydrate Changed before catalysis.	First rise.	Second rise.	Diff.	Heat of passage.
1002	1040	29.6	17.8	0.5	0.033	0.016	0.017	1.02
999	1038	31.3	18.8	0.6	0.028	0.012	0.016	0.91
999	1037	37.1	22.3	1.1	0.029	0.008	0.021	1.03
1000	1038	22.5	13.5	0.9	0.022	0.011	0.011	0.90
1004	1042	32.9	19.7	1.4	0.027	0.010	0.017	0.97

It appears from these measurements that the heat of passage is small, the average value being closely one calorie of heat developed for each gram of hydrate that changes in solution to β-anhydride. Brown and Pickering[1] give +0.19 as the heat developed when 1 gram of dissolved hydrate changes to the equilibrium mixture, but this is evidently a misprint and should read 0.25, which would give 0.4 calorie for the heat of passage, a value not greatly different from the one here found. It is exceptional that the formation of this anhydride should develop heat,

[1] *Loc. cit.*, p. 782.

solutions to reach equilibrium, and a mixture of strong alcohol and ether is then added, a crystalline precipitate is formed which does not show mutarotation when it is dissolved in water as do the other forms of milk-sugar. Tanret[1] who discovered this precipitate in 1896 regarded it until recently as a new form of milk-sugar, the stable modification to which the other forms revert in solution, ascribed to it the formula $C_{12}H_{22}O_{11}.\frac{1}{2}H_2O$, and named it β-lactose. It is now generally accepted that this form is a mechanical mixture of hydrated and β-anhydrous milk-sugar in about the proportions in which they are present in solution in equilibrium. The view that this form of milk-sugar is such a mixture was expressed six years ago[2] and direct evidence was given to support it; but as the publication in which this evidence appeared had small circulation the data are presented again, using, however, the more accurate values of the heat of solution that are now at hand. If the alcoholic precipitate is a mixture of hydrated and β-anhydrous milk-sugar its initial heat of solution will be intermediate between those of its constituents. The exact value can be calculated from the fact that the two forms must be present in the mixture in the same proportion in which they occur in the stable solution or otherwise the precipitate would show mutarotation when dissolved. It has been shown from solubility measurements[3] that this proportion at room temperature is 1.5 parts β-anhydride to each part hydrate; the initial heat of solution of such a mixture is therefore calculated to be $-[12.0 + (2.4)(1.5)] \div 2.5 = -6.2$ calories. Magie and Hudson[1] found by experiment the value -6.5 calories for Tanret's alcoholic precipitate. The agreement of these values is clear evidence that this precipitate is a mechanical mixture of hydrated and β-anhydrous milk-sugar.

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[1] *Loc. cit.*, p. 782.

The Final Heat of Solution of Hydrated Milk-Sugar Calculated from Its Solubility.—By the principles of the osmotic theory of solutions it is possible to calculate the heat of solution of milk-sugar from the change of its solubility with the temperature. The final solubilities of the hydrate are known at 15° and 25° and the final heat of solution is also known at 20°, so that a comparison of the conclusions of the two independent methods of measurement is possible. The values[1] for the solubility are 49.7 millimols per 100 grams water at 15° and 63.4 at 25°, and the molecular heat of solution (Q) is, from the well-known formula of van't Hoff, log. nat. 63.4/49.7 = Q/(1/288–1/298), equal to —4130 calories. Since the molecular weight of hydrated milk-sugar is 360, the final heat of solution per gram is —11.5 calories. This calculated value agrees perfectly with that given by the calorimetric measurement, —11.4.

Summary.

1. Each of the three forms of milk-sugar shows two heats of solution according as the rate of the balanced reaction that occurs in milk-sugar solutions proceeds very slowly or very rapidly. In the former case the initial heat of solution is observed, in the latter the final heat of solution, which is the sum of the initial heat of solution and the heat generated by the rapidly progressing reaction, called the heat of passage.

2. The following data on these heat effects at 20° have been determined with a calorimeter.

	Hydrated milk-sugar.	α-Anhydride.	β-Anhydride.
Initial heat of solution.....	—12.0 cal. gram	+7.3[2]	—2.3
Final heat of solution.....	—11.4	+7.9	—2.7
Heat of passage to β-anhydride	+ 1.0	+1.0	..

3. The equality of the heat of passage of the hydrate and the α-anhydride is further evidence supporting the accepted view that the α-anhydride passes instantly to hydrate when dissolved, which then slowly builds β-anhydride according to the balanced reaction

$$\underset{\text{(Hydrate.)}}{C_{12}H_{24}O_{12}} \rightleftarrows H_2O + \underset{\text{(}\beta\text{-Anhydride.)}}{C_{12}H_{22}O_{11}}$$

4. Evidence from two independent sources shows that the initial heat of solution of the hydrate increases about 0.1 calorie per degree rise in temperature.

5. The dilution of strong milk-sugar solutions (0.5 molal) causes a very slight development of heat, which cannot be due to any change in the equilibrium of the balanced reaction with concentration because the heat development at room temperature on dilution is instantaneous while any change of the balanced reaction at this temperature would be very slow.

[1] THIS JOURNAL, 26, 1072 (1904).

[2] From the work of Jorissen and Van der Stadt, *loc. cit.*

The heat of solution is independent of the concentration when this is less than about 0.3 molal.

6. Pure β-anhydrous milk-sugar has been prepared by an improved method of slow crystallization, and a delicate test shows that it is free from hydrate. Its specific gravity at 20° is 1.59, that of the hydrate being 1.54.

7. The present data on the heats of solution confirm quantitatively the view that the crystalline substance which alcohol and ether precipitate from cold stable milk-sugar solutions is not a pure substance as was first supposed but is a mechanical mixture of the hydrate and the β-anhydride. It does not show mutarotation when redissolved in water because the two substances are present in it in the same proportions approximately in which they occur in stable solutions.

8. When the temperature of a stable solution of milk-sugar is suddenly changed a slight thermal lag is observed in its rotatory power, which indicates that the hydration is slightly increased with rise of temperature between 0° and 100°. The direction and magnitude of this lag agree with the conclusions drawn from the observed value of the heat of passage.

9. The final heat of solution of hydrated milk-sugar is calculated from the solubilities at 15° and 25° to be —11.5, agreeing with the calorimetric measurement at 20°, which gives —11.4.

UNIVERSITY OF ILLINOIS,
URBANA, ILL.

A NEW INSTRUMENT FOR REDUCING GAS VOLUMES TO STANDARD CONDITIONS.

BY GRANT T. DAVIS.

Received April 1, 1908.

The necessity for making a considerable number of accurate measurements of gas volumes has led to the working out of the following device for their reduction to standard volume. Since all that is necessary for the physical reduction of a gas to standard volume, is to subject it to a definite pressure, a water column of variable length was first tried, but this was discarded in favor of a column of known length with a fixed scale. The length of the column of mercury (L_m) necessary to compress a gas to standard volume at temperature "t" is found by the formula, $V = \frac{v(p-p')}{760(1+at)}$, the conditions being such that $v = V$; then $p = 760\,(1 + at) + p'$ and $L_m = p - 760$. The length for the water column was taken as $L_m \times 13.59$, and correction was made for the expansion of water with rise in temperature.

The apparatus for use with gases which can be collected over water consists of a piece of iron pipe about two meters long, fitted with a T near the top and an elbow at the lower end. The elbow is closed by a rubber

stopper carrying a glass T, one arm of which is fitted with a stopcock, and the other connected to the water supply. The T at the upper end of the pipe carries a small reservoir at the top to prevent overflow in case of too hasty filling, and the side-opening is closed by a rubber stopper carrying a siphon with a very short inner leg, and the long leg emptying into the sink, or as shown in the figure. To the lower part of the pipe is attached a scale, so graduated in degrees that the column of water from the n of the short leg of the siphon to aduation is the calculated length for mperature represented by the gradua- Attached to this "temperature" scale, liding "pressure" sale whose divisions .6 mm. long.

avoid the error which would be intro- by using tap water of a temperature nt from that of the room, the system ttles "A" "B" is introduced. "A" ns distilled water at the room tem- re. Tap water being admitted to the water from "A" is forced into pparatus, and no temperature change .

use the apparatus the burette con- g the gas is connected to the T at the n of the pipe and the stopcock opened.

care must be taken that there is no air in the connecting tube. The graduation 760 on the pressure scale is placed opposite that point on the temperature scale which corresponds to the observed temperature, water is admitted to the pipe until the siphon begins to act, and while a slow stream continues to flow, the meniscus in the burette is brought level with that graduation of the pressure scale which corresponds to the observed barometric pressure, and the corrected volume of the gas read off. The position represented in the figure is that for a gas observed at a temperature of 21.4°, and barometric pressure of 754 mm.

Table "A" gives the length of water column necessary to compress a gas to the standard volume for temperatures from 15° to 34°. Table "B" offers a comparison between the standard volume as calculated, and as observed by means of this instrument.

TABLE "A."

T.	cm.	T.	cm.
15	73.9	25	126.9
16	79.2	26	132.7
17	84.0	27	138.7
18	89.2	28	144.4
19	94.2	29	150.7
20	99.5	30	157.0
21	104.8	31	163.3
22	110.2	32	169.8
23	115.8	33	176.7
24	121.2	34	183.4

TABLE "B."

p.	t.	v.	(Cal.)	V (Obs.).
750.5	20.6	42.0	37.64	37.7
750.5	21.4	41.6	37.13	37.1
742.1	26.2	41.9	36.11	36.1
742.1	26.5	31.6	27.16	27.1
741 2	26.0	30.6	26.33	26.3
733.2	21.1	74.0	64.58	64.5
736.4	22.6	6.2	5.39	5.4
748 4	19.0	50.2	45.20	45.2
760.5	18.5	49.6	45.51	45.4
760.0	21.0	41.7	37.77	38.8

UNIVERSITY OF ILLINOIS,
URBANA, ILL.

A LECTURE TABLE DOWN-DRAFT.

BY WM. L. DUDLEY.

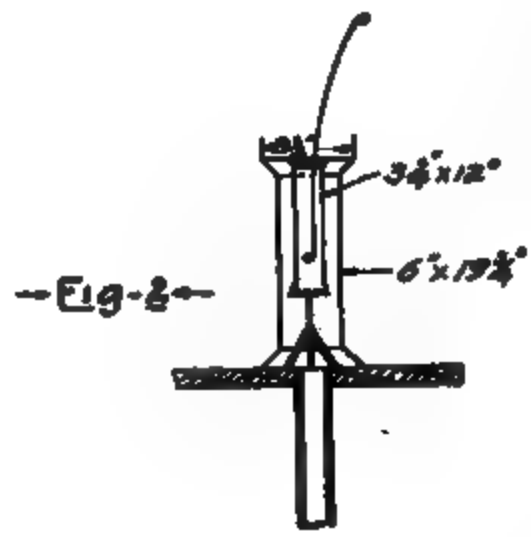
Received March 26, 1908.

A powerful and reliable down-draft on a lecture table is of great service and is much superior to a hood behind the lecturer since by its use experiments with the most disagreeable and poisonous gases can be made safely in full view of the audience.

My experience in the past has been that such down-drafts are rare, in fact, I have never had one that was usable until I installed in the lecture theatre of Furman Hall, the new chemical laboratory, the arrangement herein described.

The requirements of a good down-draft are (1) certainty of action regardless of the weather or temperature, (2) sufficient suction to permit of moderate freedom of action on the part of the experimenter which is not possible if the air current is so slow as to require a closed chamber to prevent the escape of gases into the room, (3) the draft tube with its cover being so arranged that it can be located in or near the center of the lecture table flush with the table top so as to offer no obstruction, and (4) a cover to the draft tube which will not stick nor become fast from corrosion.

All of these requirements are amply met by our down-draft arrangement which will be readily understood by reference to the accompanying sketch and description.



A (Fig. 1) is the top of the lecture table. B is a two-inch cast iron soil pipe which drops vertically through the lecture table and the floor under which it passes at right angles to a flue. The end of the horizontal pipe is closed at D by a plug, through the center of which passes a brass pipe, E, one-eighth of an inch inside diameter, extending about 12 inches beyond the vertical pipe. The pipe E is connected to a compressed air pipe.

The hub of the vertical pipe B is fitted with an ordinary two-inch brass "wash-tray plug," without a stopper, set flush with the table top by letting it into the wood. Connected with the crossbars in the wash-tray plug is a chain, the other end of which is attached to the bottom of a thin flat brass plate, F, $2\,^{5}/_{16}$ inches in diameter, which serves as a cover. This cover fits flush with the wash-tray plug which has had an offset turned in the face, of sufficient diameter to receive the cover-plate. A finger lift is also cut in the plug, thus the cover plate can be easily slipped aside when the down-draft is in use and the chain prevents its being detached. The valve controlling the supply of compressed air is located under the table at a place most convenient to the experimenter.

In using the down-draft, I perform the experiments inside of a glass cylinder six inches in diameter and open at both ends, as shown in Fig. 2. At one end, the cylinder is 8½ inches in diameter and at the other, 10 inches in diameter. The vessel containing the gas or volatile substance is placed on an adjustable support over the down-draft pipe, and the glass cylinder is put around it with its larger end resting on the table.

The top of the vessel, for convenience, should be about on a level with the top of the cylinder. When the vessel is opened all of the fumes which come out are sucked down into the down-draft pipe.

With an air pressure of 25 pounds, the suction in the down-draft tube is 2¼ inches of water pressure, and the velocity of the air going through the six-inch cylinder was found by careful anemometer measurement to be 135 feet per minute, which gives a velocity of about 1200 feet per minute in the two-inch down-draft pipe.

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PURITY AND VOLATILITY OF PRECIPITATED ANTIMONY SULPHIDE.

BY LEWIS A. YOUTZ.

Received April 10, 1908.

This work was taken up to discover whether pure antimony trisulphide could be obtained by precipitation by hydrogen sulphide. The volatility of the product of precipitation when heated in an inert atmosphere came in more or less incidentally in the course of the work as a check on the purity of the sulphide. Practically the only impurity considered however was the chloride.

Most of the work on the determination of antimony by precipitation as sulphide, as is too often the case in analytical work in general, is empirical. The investigator will fall upon a method that approximates accurate results; then by shifting the conditions here or there he finally arrives at a set of conditions that will give results within the limits of experimental error. He then announces his method as an accurate one though often it is accurate merely because of a series of compensating errors.

It might be said in anticipation that such was found to be the case in the method of determining antimony by precipitation as sulphide in the presence of hydrochloric acid, heating the dried sulphide in an atmosphere of carbon dioxide, and weighing.

Purity.

(1) As a preliminary experiment in the investigation of the purity of the precipitated sulphide, two samples of antimony trichloride of approximately 1.5 grams each were dissolved in 250 cc. of water and 30 cc. of concentrated hydrochloric acid, the antimony precipitated as completely as possible by hydrogen sulphide gas, the volume of the liquid then increased to 500 or 600 cc., warmed nearly to boiling, and saturated with the gas. The sulphides were washed with water saturated with hydrogen sulphide till 10 cc. of wash water gave no test for chloride, or but a faint trace. It should be noted that it is very difficult to wash the precipitated sulphide free from chloride, from 1000 to 1500 cc. of water being required in this and

in subsequent cases where precipitation was made in the presence of hydrochloric acid. These precipitates were tested qualitatively, and notable quantities of chloride were found in each.

The method of testing for chloride in this case as in all subsequent cases was to fuse the sulphide in sodium carbonate in a porcelain crucible, acidify the fusion with sulphuric acid after taking up with water, filter out the sulphide produced by the acidification and test the filtrate for chloride after the removal of any hydrogen sulphide in the solution. Blanks were run in every case, as sodium carbonate absolutely free from chlorides was found extremely difficult to obtain or to make. Testing for chlorides by making a solution of the trisulphide by means of concentrated sulphuric or nitric acids, was not thought wise, owing to the liability of volatilization of the chloride by the acid, and also owing to the interference in precipitation of chloride by silver nitrate in the presence of antimony. A crucible was tested for chloride by fusion of sodium carbonate in it. No chloride was found. The glaze did not contain chloride.

(2) Thinking that taking a smaller amount of antimony chloride to start with, so as to give less of the sulphide to wash, might effect the amount of chloride in the end, 0.2215 gram of metallic antimony was dissolved in aqua regia, the solution boiled with excess of hydrochloric acid till the nitric acid was decomposed, ending with about 50 cc. of 20 per cent. hydrochloric acid. This was then diluted with about 400 cc. of water and the antimonic acid treated with hydrogen sulphide till complete precipitation of antimony pentasulphide. The precipitate was then washed till no further test for chloride was found in the filtrate. A sample of the precipitate showed abundant chloride present.

(3) 0.2400 gram of metallic antimony treated as the preceding, but the precipitate dried to constant weight at 110°, was heated for 0.5 hour to 240–250° in an atmosphere of carbon dioxide. This precipitate, assuming it to be antimony trisulphide calculated over to antimony, indicated 0.2397 gram antimony. It will be noted that the sample of sulphide was heated to 250° in an atmosphere of carbon dioxide, and the results showed only 0.12 per cent. error, yet on testing a strong test for chloride was indicated. The antimony was oxidized to the pentad form and precipitated as pentasulphide, with the thought that the sulphur freed from this sulphide, when transformed to the black modification and triad antimony sulphide, might act to transform any chloride of antimony to the sulphide at the higher temperature.

(4) A sample of 0.3251 gram of antimony sulphide precipitated from a hydrochloric acid solution as usual and dried at 110° to constant weight gave 0.3 per cent. chlorine equivalent to 1.45 per cent. SbOCl, supposing the chloride to be in this form under the conditions.

(5) To try the effect of tartaric acid on reducing the amount of adherent

chloride, a sample of antimony sulphide was prepared from metallic antimony as in the previous cases but 5 grams of tartaric acid were added before precipitation. The precipitate was washed as usual and dried at 110°. 0.2954 gram of this sulphide gave, on testing, 0.51 per cent. chlorine equivalent to 2.47 per cent. SbOCl. Another portion of this heated 0.5 hour at 240° gave 0.242 per cent. chlorine, which, if considered as $Sb_4O_5Cl_2$ as is the case when pure antimony oxychloride is heated to 250°, is equivalent to 1.80 per cent. $Sb_4O_5Cl_2$. 247 grams of SbOCl by loss of $SbCl_3$ to become $Sb_4O_5Cl_2$ by calculation give 184 grams of $Sb_4O_5Cl_2$, which points strongly to the impurity being $Sb_4O_5Cl_2$ after being heated to 250°. Plainly here the tartaric acid did not reduce the amount of chloride as impurity.

(6) Another sample treated as in the preceding case, but with the tartaric acid omitted, gave chlorine 0.66 per cent. on the sulphide dried at 110°, but 0.45 per cent. after being heated to 240° for 0.5 hour.

(7) A sample from 0.2680 gram of antimony dissolved as usual in aqua regia, precipitated by hydrogen sulphide, washed as usual, precipitate dissolved in ammonium sulphide, reprecipitated by acetic acid, dried at 110°, heated in intervals of 0.5 to 1.5 hours in carbon dioxide for a total of nine hours, showed 0.10 per cent. chlorine yet present which is equivalent to 0.9 per cent. $Sb_4O_5Cl_2$.

These samples of results represent only a few of a much larger number of experiments carried out with varying amounts of antimony and hydrochloric acid present. In no case was it found possible to produce a precipitate of antimony sulphide, either the trisulphide or the pentasulphide, even approximately free from chloride, nor was it possible to remove the chloride by washing, though a point could be reached after long washing where the wash water contained but the merest trace of chloride. Yet these samples contained as high as 2.47 per cent. of chloride calculated as SbOCl, and in one case after heating for 0.5 hour in a carbon dioxide stream to 250°, showed 4.05 per cent. calculated as $Sb_4O_5Cl_2$.

The tartaric acid was without apparent effect in reducing the amount of chloride retained by the precipitate. Further, it was surprising that after dissolving the precipitated sulphide in ammonium sulphide free from chloride, and reprecipitating by acetic acid also free from chloride, the sulphide yet contained chloride, and after heating for 9 hours to 250 degrees there was still present 0.10 per cent. chlorine.

Volatility of the Precipitated Sulphide.

A large number of tests of the volatility of these sulphide precipitates were carried out under varying conditions of precipitation. Uniformly the precipitates were heated in an atmosphere of carbon dioxide at a temperature of approximately 250° after drying to constant weight at usually 105–110° in air.

The precipitated sulphides were collected and washed in a Gooch cruci-

ble with asbestos filter. After drying the precipitates in the crucible, they were in each case placed in a small beaker covered with a watch glass perforated to admit a thermometer and carbon dioxide delivery tube. The beaker and crucible so arranged were then heated in an asbestos oven after the removal of the air from the beaker by carbon dioxide.

A few only of the tests will be given as illustrations:

(1) 1.5 grams of antimony chloride were dissolved in water and enough hydrochloric acid added to give a clear solution, the antimony precipitated by hydrogen sulphide, filtered, washed till the wash water was free from chloride and dried in air at 110°. This sample was heated at varying intervals of from 1 to 5 hours in an atmosphere of carbon dioxide at a temperature of 250°, altogether for 34 hours. The loss on approximately 1 gram of the precipitate averaged 1.1 mg. per hour though the loss per hour was somewhat irregular. The last hour it lost 2.5 mg.

(2) A sample of 0.1931 gram metallic antimony was dissolved in aqua regia, excess of nitric acid decomposed by boiling with hydrochloric acid, diluted and precipitated as usual. After heating for 1 hour at 230° the sulphide calculated over to antimony indicated 0.1936 gram antimony; results were thus quantitative so far. After heating for 1.5 hours more the weight was reduced by 5.8 mg., or something over 2 per cent. loss.

(3) To test the volatility of the sulphide free from chloride a gram of tartar emetic purified by crystallization was dissolved in water and precipitated after acidification with a small amount of sulphuric acid and a larger amount of acetic acid. The precipitate after drying at 110° weighed 0.4942 gram. After heating for 3 hours at 250° it weighed 0.4938. Loss 0.4 mg. Thus the sulphide free from chloride is practically non-volatile.

(4) Another sample of 0.1810 gram of antimony was dissolved and precipitated as usual. The sulphide was then dissolved by ammonium polysulphide and reprecipitated with dilute sulphuric acid. This was repeated three times. Finally the precipitate was washed, thoroughly dried and heated to 250° as usual. After the first large loss due to the sulphur from the pentasulphide, 2.5 hours' heating in three intervals caused a loss of 1.7, 2.6, 2.7 mg. successively.

As was shown by a quantitative test for chloride in another sample similarly treated, the remarkable thing here is the persistency with which the chloride is retained by the precipitated antimony chloride, for it is the presence of chloride that causes the volatility.

These illustrations are ample to show the impossibility of getting constant weight at 250° with chloride present.

Is the method accurate? It is almost useless to discuss this question for the method of precipitating antimony as sulphide, either trisulphide or pentasulphide, transforming to the black modification, and volatiliza-

tion of the excess of sulphur in an atmosphere of carbon dioxide at 250° has long been used with good results for accuracy in the hands of many analytical chemists.

But merely to bring the fact freshly to our minds again, I give here a dozen or more determinations made by starting with metallic antimony, with the temperature, time of heating in carbon dioxide atmosphere, and the acid used.

Wt. of Sb.		Temp.	Time, hrs.	Sb found.
0.1931	HCl acid	227°	0.5	0.1936
0.2040	" "	245°	0.5	0.2037
0.2287	" "	240°	0.5	0.2283
0.3685	" "	250°	0.5	0.3692
0.1414	" "	245°	0.5	0.1415
0.2400	" "	240°	0.5	0.2397
0.2586	HCl and Tar. acid	240°	0.5	0.2584
0.2405	" " " "	240°	0.5	0.2409
0.2035	" " " "	250°	0.5	0.2031
0.2060	" " " "	245°	0.5	0.2066
0.1592	" " " "	250°	0.5	0.1596
0.2214	" " " "	240°	0.5	0.2221

This is sufficient to show that quantitative results may be obtained. In no case is the error over 0.3 per cent. and usually from 0.1 to 0.2 per cent. even when calculated to metallic antimony, which is clearly close enough for any ordinary analytical work. To be sure, if the samples were to be heated much longer than 0.5 hour the error would rapidly increase and soon would become large owing to the volatility of the chloride.

It is not surprising that the results should be quantitative when the sulphide is heated only for a short time just long enough to volatilize the sulphur either free or combined as pentasulphide and to transform the sulphide to the black modification, for the equivalent molecular weights for Sb_2S_3—SbOCl and $Sb_4O_5Cl_2$ are 168.2, 171.45 and 157.9 respectively and thus not very widely apart, so that as far as the weight of the precipitate is concerned even several per cent. of SbOCl or even $Sb_4O_5Cl_2$ as an impurity would give a weight practically the same as though the antimony were all in the form of sulphide.

I am greatly indebted to Mr. Alva G. Austin for carrying out much of the detail of this work.

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A SCHEME FOR THE SEPARATION OF THE RARE EARTHS.

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In this communication, a comparatively simple scheme for the separation of mixtures of the rare earths is offered in the hope that it may prove of

value to any one who is desirous of entering this very interesting field of research. The conclusions presented are the results of several years' investigation upon the various methods proposed for fractionation and of personal trial of the applicability of many other compounds which had not previously been employed for the separation of these elements. Only those methods which proved valuable will be mentioned.

It might be as well to state in the beginning for the benefit of those who have had little cause to study this subject, that there is no quantitative method for the separation of any of the rare earths. The true members of this family comprise those elements that are included in the cerium and yttrium groups and are characterized by their trivalency and by the fact that they form oxalates that are insoluble in dilute acids and in cold ammonium oxalate solution.

The nearest approach to a quantitative separation is found in the case of cerium. This is due to the fact that the properties of the metals of all these earths and their salts, with the possible exception of cerium itself, vary among themselves by very minute differences.

Bearing these observations in mind, the following scheme is presented: The mineral is decomposed, either by hydrochloric acid, sulphuric acid, potassium bisulphate, sodium hydroxide or hydrofluoric acid. When hydrochloric acid is used, the whole is evaporated to dryness to render the silica insoluble. It is then warmed with a little concentrated hydrochloric acid, after which the mass is treated with water and filtered. The filtrate may then be treated with either oxalic acid or ammonium oxalate. If the liquid contains considerable mineral acid, ammonium oxalate is to be preferred. When sulphuric acid or potassium bisulphate has been used to break up the mineral, it is necessary to stir with *cold* water to obtain the solution of the desired elements. Fusion with sodium hydroxide and washing with water gives a residue of oxides. These are dissolved in hydrochloric acid. Hydrofluoric acid decomposes many minerals, such as columbates, tantalates, etc., in the cold, giving a residue of rare earth fluorides while silicon, columbium, tantalum, etc., go into the solution. The insoluble fluorides are decomposed by means of sulphuric acid.

In the sulphate or chloride solutions obtained by one of the above methods, the earths are then precipitated by ammonium oxalate or oxalic acid as mentioned above.

Having obtained the earths in the form of oxalates, they are treated as follows:

Zirconium and Thorium.—Should the rare earth oxalates contain these elements they may be separated by boiling with a solution of ammonium oxalate when the whole of the zirconium and nearly all of the thorium pass into solution. The residue is filtered off and washed

with ammonium oxalate solution. On the addition of an excess of hydrochloric acid to the filtrate, thorium oxalate alone is precipitated, while the whole of the zirconium is held in solution by the oxalic acid produced by the action of the hydrochloric acid on ammonium oxalate.

As zirconium oxalate is soluble in an excess of oxalic acid, this reagent alone may be used in the absence of thorium. In this connection it should be remembered that the oxalates of cerium and of the earths of the yttrium group, are somewhat soluble in hot concentrated ammonium oxalate solution so that varying amounts go into the solution. Thorium, however, can be separated easily from the yttrium earths which remain with it, by means of the double sulphate of thorium and potassium, which is insoluble in a solution of potassium sulphate, while the corresponding compounds of the yttrium group are soluble. The crude thorium oxalate is converted into sulphate and the cold solution is stirred with solid potassium sulphate. Sulphate solutions of the earths are the best to work with for this purpose, for if other compounds are used, care must be taken to keep the solution from being too concentrated since members of the yttrium group may be precipitated also.

After the removal of the yttrium earths, cerium earths are still present and thorium may be separated from these by means of the solubility of its oxalate in ammonium oxalate or, according to Glaser, by the solubility of thorium oxalate in ammonium acetate;[1] also by the method of Wyrouboff and Verneuil in which thorium is precipitated by hydrogen peroxide.[2] These methods are given under the separation of cerium and thorium, because under usual conditions they separate together from the rest of the rare earths.

In the next step, there are three alternatives which depend upon the composition of the oxalates as approximately determined from the solubility of the double sodium or potassium sulphates in potassium or sodium sulphate solution, *viz.*, (*a*) if containing 20 per cent. or more of the yttrium earths and only a trace of thorium; (*b*) if containing 20 per cent. or more of the yttrium earths together with thorium; (*c*) if containing less than 20 per cent. of the yttrium earths.

(*a*) When the material consists of 20 per cent. or more of the yttrium earths and practically no thorium, the oxalates are converted into sulphates by mixing with strong sulphuric acid and carefully igniting until fumes of sulphuric acid are no longer evolved. The residue is then powdered and dissolved in *ice-cold* water. The resulting sulphate solution is stirred with solid sodium sulphate which throws down the double sulphates of sodium and the cerium earths.[3]

[1] THIS JOURNAL, 18, 782.

[2] *Bull soc. chim.* [3], 19, 219.

[3] Another method, which is simpler if the oxides will dissolve in acid, is to ignite

This precipitate contains some of the yttrium group of earths, while small amounts of samarium, gadolinium and europium remain in solution. The precipitate is separated by filtration and washed with a solution of sodium sulphate. The insoluble double sulphates consist chiefly of cerium, lanthanum, praseodymium, neodymium, samarium, europium and gadolinium together with small amounts of the yttrium earths in which the terbium, dysprosium and holmium contents are considerably increased. These double sodium sulphates constitute Fraction *A* of the table. The filtrate, on the addition of an excess of oxalic acid, throws down the oxalates of terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium and scandium together with some samarium, europium, and gadolinium. This precipitate forms Fraction *B* of the table.

(*b*) The composition of the oxalates in this case is very similar to (*a*), the only difference being the thorium content.

The sulphate or chloride solution is treated with sodium sulphate and the insoluble double sodium cerium group sulphates, forming Fraction *A*, filtered off. Since the sodium thorium sulphate is somewhat soluble in sodium sulphate solution, the filtrate is saturated with potassium sulphate, when the remaining thorium is precipitated as thorium potassium sulphate, insoluble in potassium sulphate solution. After separating the precipitate, the filtrate is treated with an excess of oxalic acid, the insoluble oxalates being filtered off and washed. This material is added to Fraction *B*.

(*c*) In this, the third and last alternative, the oxalates consist almost entirely of the cerium metals, and it is best to start the work of separation from the point *A*.

Cerium and Thorium.—The next operation consists of separating cerium together with thorium, if the latter is present, from the other elements forming Fraction *A*. This is best carried out by treating the nitrate solution with an excess of zinc oxide and potassium permanganate. If the material is in the form of the insoluble double sodium sulphates, it should be boiled with sodium hydroxide in excess. The resulting hydroxides are filtered off, well washed with hot water and dissolved in nitric acid. In dealing with oxalates that contain large amounts of lanthanum, praseodymium and neodymium, it is necessary only to ignite when the oxides, so obtained, will readily dissolve in nitric acid. As a

the oxalates and dissolve the oxides so obtained in hydrochloric acid or nitric acid, dilute the solution and treat with solid sodium sulphate until the double sulphates are precipitated. However, when oxalates rich in cerium are ignited, the oxides which are formed dissolve with great difficulty in hydrochloric or nitric acid and so in this case it is better to treat the oxalates with sulphuric acid as mentioned above. Extra care must be taken when the chlorides or nitrates in solution are stirred with solid sodium sulphate, for if the solution is too concentrated, metals from the yttrium group will be precipitated also.

rule, when cerium is present in large amounts, since the oxide dissolves with great difficulty, the oxalates are converted into sulphates. The sulphate solution is then poured into fairly strong and boiling sodium

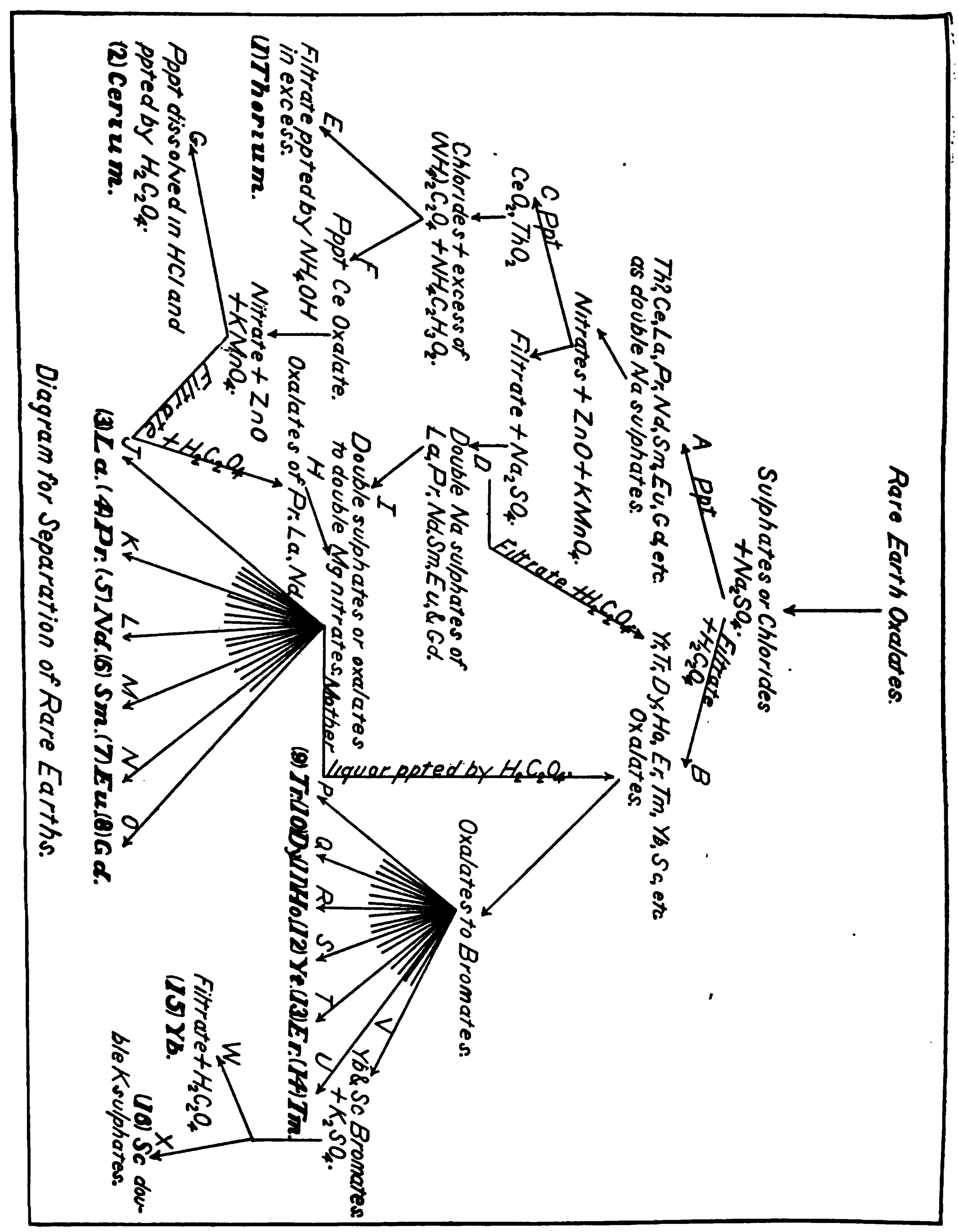

Diagram for Separation of Rare Earths.

hydroxide. The rare earth hydroxides formed under these conditions filter rapidly, and after washing with boiling water, are dissolved in nitric acid. The nitrate solution obtained by any of the above methods is neutralized, stirred rapidly by a motor and an *excess* of zinc oxide added. On the addition of potassium permanganate, cerium peroxide is precipitated and the addition is continued until the liquid after continued stirring remains red. This method leaves a little cerium in solution, which is separated later. The precipitate, consisting of cerium and manganese peroxides together with thorium and a small amount of lanthanum, praseodymium and neodymium, makes Fraction *C* on the diagram. The filtrate is saturated with sodium sulphate, causing a precipitate of the double sulphates of sodium with lanthanum, praseodymium, neodymium, etc. This, after filtering and washing with sodium sulphate solution, constitutes Fraction *D*. To this last filtrate, containing small amounts of the yttrium group, an excess of oxalic acid is added. The oxalates so obtained are united with those forming *B*.

Thorium.—Although thorium is not now considered as a rare earth, methods for its purification do not seem to be altogether out of place. The cerium peroxide contains large amounts of manganese, which is first removed by dissolving in strong hydrochloric acid and precipitating the earths by means of solid sodium sulphate until no more insoluble double sulphates separate. The liquid is then filtered and the precipitate washed with sodium sulphate solution. A portion of the thorium remains in the filtrate, but this can be separated either by means of oxalic acid or else by stirring with solid potassium sulphate.

The cerium sodium sulphate is boiled with an excess of sodium hydroxide, the residue filtered off, washed with boiling water and dissolved in nitric acid. The nitrate solution is then neutralized by means of ammonia, after which peroxide of hydrogen is added[1] and the whole boiled for a few minutes. Some of the filtered solution should then be tested by treating with an equal volume of hydrogen peroxide and boiling and the process repeated until no precipitate is thus obtained. The filtrate is reserved for the preparation of pure cerium. The thorium precipitate, having the composition $Th_4O_7N_2O_5$, is very impure and may have a yellow or even an orange color after standing for a short time.[2]

The crude thorium obtained above, may be purified by treating the nitrate solution with an excess of warm ammonium oxalate. The soluble portion can then be converted into the oxalate and treated again with warm ammonium oxalate.

[1] Wyrouboff and Verneuil, *Bull. soc. chim.* [3], 19–20, No. 6 and *Chem. News*, 77, 245.

[2] It is highly important that the peroxide of hydrogen be free from phosphoric acid; otherwise an insoluble cerous phosphate may be thrown down with the thorium.

Thorium can be separated from cerium[1] by the solvent action of ammonium acetate on thorium oxalate. This as well as the ammonium oxalate method can be applied to the cerium precipitate. The whole is dissolved in strong hydrochloric acid and precipitated by means of oxalic acid. Glaser says: "Thorium is separated best by converting the oxalates into sulphates, the greater part of the free acid neutralized with ammonia, the solution boiled and boiling ammonium oxalate added in excess. After a short time (as soon as oxalates of the cerium metals have formed but before the liquid has cooled), a solution of ammonium acetate is added. When cold, the entire cerium group is precipitated as oxalates while thoria remains in solution. After prolonged standing, best over night, the insoluble oxalates are removed by filtration *F*; in the filtrate, precipitate thoria with ammonia in excess, filter and wash." All the thorium precipitates are accumulated at *E* on the diagram. Another treatment or two, with hydrogen peroxide in neutral nitrate solution, gives a very good thorium product.

Thorium can be obtained very pure in the following manner: Thorium hydroxide is first prepared by adding a slight excess of ammonium hydroxide to a solution of thorium nitrate and washing well the precipitate thrown down. This is then added to a solution of acetylacetone in absolute alcohol and the mass heated on the water bath for a short time, after which it is filtered and allowed to crystallize. The acetylacetonate is then placed in a very small retort and carefully distilled in a vacuum. The portion that condenses in the neck of the retort and in the receiver is dissolved in concentrated nitric acid, boiled for a short time, diluted with water, filtered and precipitated by means of oxalic acid. Thorium oxide obtained by igniting this oxalate is absolutely snow-white even after long ignition. A determination of the equivalent gave an atomic weight of 232.3. Thorium may also be purified by the sulphate method as follows: Anhydrous thorium sulphate is dissolved in ice-cold water until the liquid is saturated.[2]

The filtered liquid is then heated to 20° C., when nearly pure thorium sulphate separates. It is then dehydrated and the treatment repeated two or three times.

Cerium.—*F* is the starting point for the preparation of pure cerium. If Wyrouboff and Vereneuil's method for separating thorium has been used, the purification is easily carried out by slightly modifying the zinc oxide and potassium permanganate method. If other methods have been used it is best to convert the oxalates, etc., into nitrates. The liquid is neutralized by ammonia and treated with hydrogen peroxide in order to remove the last of the thorium. To the solution of cerium

[1] Glaser, THIS JOURNAL, 18, 782.

[2] According to Urbain ammonium acetate aids the solution.

nitrate, freed from thorium, sufficient ammonium nitrate is added to form the double salt. An excess of potassium permanganate is run in and only enough cream of zinc hydroxide added to precipitate most of the cerium, being sure to leave some in solution, for otherwise praseodymium and neodymium will accompany the precipitate. The whole is then heated by steam, filtered and washed with water containing a little ammonium nitrate. The precipitate is dissolved in concentrated hydrochloric acid, the solution diluted and the cerium precipitated with oxalic acid, *G*. The oxalate obtained by this method usually contains a little zinc and manganese, the latter coloring the oxide brown, so for the final purification the oxalate is treated with a slight excess of sulphuric acid and the whole heated until the fumes of sulphuric acid are no longer given off. The resulting sulphate is dissolved in cold water and the filtered solution heated on the water bath. The sulphate that separates is washed with boiling water. This material should give an oxide with only a pale yellow tint.[1]

The mother-liquor is treated with oxalic acid, the oxalate which is thrown down being worked up with the next lot. The filtrate from the cerium peroxide still contains cerium, which is removed by adding an excess of zinc oxide and more potassium permanganate should the color be discharged. The precipitate obtained here is mixed with *F*. The filtrate is precipitated with an excess of oxalic acid and the insoluble oxalates, consisting of lanthanum, praseodymium, neodymium, etc., constitute Fraction *H*.

Lanthanum, etc.—Fractions *H* and *D* contain lanthanum, praseodymium, neodymium, samarium, europium and gadolinium together with small amounts of the yttrium earths and some cerium.

These are best separated from each other by the fractional crystallization of certain double nitrates, such as those formed by the rare earth nitrates with ammonium, magnesium, manganese or nickel nitrate. For the separation of lanthanum and praseodymium the double ammonium nitrates are by far the best and for separating praseodymium from neodymium the manganese salts are to be preferred. However, where one is working on the large scale it is better to start with the double magnesium nitrates, as the more soluble portions crystallize more readily than is the case with the double ammonium nitrates.

The double magnesium nitrates,[2] $2[M'''(NO_3)_3].3[Mg(NO_3)_2] + 24H_2O$, are prepared by dissolving the rare earth oxides in a known amount of nitric acid. An equal amount of nitric acid is then neutralized by mag-

[1] Praseodymium is a very common impurity found in cerium. This has been pointed out many times by different investigators, so that if very pure cerium is required, one must be on his guard against this substance.

[2] Demarçay, *Compt. rend.*, 130, 1019.

nesium oxide, after which the two solutions are mixed and evaporated until upon blowing on the surface, small crystals form. Water is sprayed over the surface and the whole allowed to crystallize for about twenty-four hours. The mother-liquor is then poured off and evaporated further, while the crystals are heated with water until dissolved, the correct amount to use being soon learned by experience. Both fractions are again allowed to crystallize for a like period, the concentration of the solutions being such that half of the solid separates on cooling. Two fractions have thus been obtained and in subsequent fractionations the more soluble moves in one direction and the less soluble in the opposite. After the crystallization of the second series is complete the liquid from the most soluble portion is poured off and evaporated, while the liquid from Fraction *I* is used as the solvent for the crystals forming Fraction *II*, adding water or evaporating as may be necessary. The least soluble portion, Fraction *I*, is again dissolved by heating with water. The above is repeated many times. When the fractions at either end become too small to work they should miss one crystallization and then be added to the next lot. After a few series of crystallizations, the least soluble portion becomes very light colored, later growing nearly colorless, and finally takes a faint green tinge. When the fractions at this end no longer show the characteristic absorption bands of neodymium, they should be placed aside and mixed together according to the amount of praseodymium contained therein; in other words, fractions of the same color are united.

The most soluble portion changes very rapidly. It soon takes a yellow color and shows a samarium spectrum together with the bands of dysprosium, holmium and erbium. Sometimes at this stage the liquid refuses to crystallize or else a precipitate may form. If either of these things happens it is best to dilute with water and saturate with solid sodium sulphate to separate the yttrium earths and impurities that have accumulated and interfere with the crystallization. The insoluble double sodium sulphates are converted back to the double magnesium nitrates in the same manner as already described and the solution will be found to crystallize readily on evaporation. The filtrate from the double sodium sulphates is precipitated with an excess of oxalic acid and the oxalates of the yttrium group which are thrown down are added to lot *B*. The neodymium bands finally become very weak in the most soluble fractions and these are set aside for the preparation of samarium, europium and gadolinium. After the samarium has been separated in this manner the more soluble portion of the remaining fractions rapidly turns to a beautiful amethyst and when this occurs it is separated from the rest as neodymium. After the process has been continued a little longer it will be found that the material has been split up into four groups according

to the order of their solubilities. Commencing with the least soluble we have:

1. Lanthanum and praseodymium.
2. Praseodymium and neodymium.
3. Neodymium.
4. Samarium, europium and gadolinium together with small amounts of terbium, dysprosium, etc.

Lanthanum.—Lanthanum and praseodymium are best separated from each other according to the method of Auer von Welsbach[1] which consists of the fractional crystallization of the double ammonium nitrates of the type $M'''(NO_3)_3.2(NH_4NO_3) + 4H_2O$. These compounds are crystallized from water containing nitric acid to the extent of one-tenth the weight of the dissolved solid. To prepare the double salts, the oxides are dissolved in the required amount of nitric acid and for every three parts of acid required for the oxides two additional parts are neutralized by ammonium hydroxide. The resulting solutions are mixed, filtered and evaporated until small crystals form on blowing over the surface of the liquid. A little water is sprayed over the surface and the whole set aside for twenty-four hours. The process of fractionation is then carried out similarly to the double magnesium nitrates. By this method lanthanum ammonium nitrate is soon obtained perfectly colorless and a saturated solution gives no praseodymium absorption spectrum even when observed through very thick layers. The lanthanum ammonium salt does not enclose anything like the amount of mother-liquor that the double magnesium compound does. Both cerium and praseodymium accumulate in the more soluble portion.

The colorless lanthanum salt is dissolved in water, the solution acidified and precipitated by means of oxalic acid. This oxalate is treated with a slight excess of concentrated sulphuric acid and the whole gently ignited until all free acid has been driven off. The sulphate is powdered and dissolved in water at about 1° until the liquid is saturated, after which it is filtered, placed in a water bath and gradually raised to 32°. The solution soon changes to a solid mass which is placed on a Buchner funnel and washed with hot water. The few grams that remain in solution are thrown out by means of oxalic acid. The crystallized sulphate may be rendered anhydrous and submitted once again to the sulphate method.

This lanthanum gives a fine white oxide.

Praseodymium.—There are two sources for praseodymium, firstly, from the more soluble portion obtained from the purification of lanthanum and secondly, from those fractions of the double magnesium nitrates which show a strong praseodymium spectrum. These are not mixed but treated separately.

[1] *Monatsh. Chem.*, 6, 477

In the first case the crystallization is carried on until no more colorless crystals separate, praseodymium accumulating in the more soluble fractions together with a little cerium.

In the second case the double magnesium salts are converted into the corresponding manganese compounds which are finally fractionally crystallized[1] from nitric acid of sp. gr. 1.3. In order to do this the magnesium double salts are dissolved in water, the solution acidified and the rare earths thrown down by oxalic acid. The oxalates obtained are washed, dried and ignited to oxides. The oxides are then dissolved in a known amount of nitric acid. An equal amount of nitric acid is then neutralized by manganese carbonate, after which the two solutions are mixed. A precipitate of manganese peroxide is sometimes obtained at this point but it is easily removed by adding a little oxalic acid and warming. The least soluble portion, from this fractional crystallization that no longer gives any neodymium bands in the spectroscope, is dissolved in water, acidified and thrown down with oxalic acid. The fractions of praseodymium ammonium nitrate that are free from lanthanum are also dissolved and precipitated by oxalic acid. The praseodymium oxalate from the two sources is then united. This material may be impure, owing to the presence of cerium.

Cerium can be separated in several different ways. One method consists in treating the nitrate solution with potassium permanganate and a little sodium carbonate. A separation is obtained according to Wyrouboff and Verneuil[2] by adding a solution of sodium acetate to a solution of the nitrates and precipitating the cerium by hydrogen peroxide. The above methods throw down a certain amount of praseodymium also, so the precipitate should be worked up again.[3]

Neodymium.—Pure neodymium is obtained by continuing the crystallization of the neodymium magnesium nitrate obtained somewhat earlier. After a few more series of crystallizations the liquid assumes a beautiful bluish lilac color which is seen better when some of the solution is diluted with water. On observing the spectrum the absorption bands in the blue stand out clearly. When the solution contains samarium or praseodymium, these weaker neodymium bands are usually a little hazy. An excellent test of the purity of neodymium is found by observing the color of the oxide which is blue only when pure.

Samarium and Europium.—Samarium, europium and gadolinium are contained in the mother-liquors which are obtained during the fractionation of the double magnesium nitrates. The solutions are evaporated

[1] Lacombe, *Bull. soc. chim.* [3], **31**, No. 10 and *Chem. News*, **89**, 277.

[2] *Bull. soc. chim.* [3], **19**, No. 6 and *Chem. News*, **77**, 254.

[3] Meyer and Koss, *Ber.*, **35**, 672, recommend magnesium acetate in place of sodium acetate.

and the residue fractionally crystallized from nitric acid[1] of 1.3 sp. gr. The addition of the isomorphous bismuth magnesium nitrate aids enormously in the separation of these elments as Urbain and Lacomb[2] have shown. Its solubility places it between samarium and europium and it also assists in the crystallization of the sirupy mother-liquors inasmuch as it carries down with it the more crystallizable portions. Samarium is obtained from the least soluble fractions. Europium is separated from the excess of bismuth magnesium nitrate which is found between the samarium and gadolinium fractions. The bismuth is thrown down by hydrogen sulphide and the mother-liquor precipitated by means of oxalic acid.

Gadolinium.—The fractions between europium and dysprosium, etc., consist mainly of gadolinium magnesium nitrate. These solutions are acidified and the gadolinium thrown down as oxalate. This is then washed and ignited to oxide. The resulting oxide is converted into the nickel nitrate[3] of the type $2Gd(NO_3)_3.3Ni(NO_3)_2 + 24H_2O$, which is then fractionally crystallized from nitric acid of density 1.3. Terbium is left in the most soluble portion.[4]

Fraction *B* contains oxalates of terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium and scandium. This material is converted into the anhydrous sulphate, the latter dissolved in cold water and poured over an excess of barium bromate.[5] The whole is well stirred and placed on the water bath. After the double decomposition is complete, *i. e.*, when the clear liquid gives no precipitate with barium bromate solution after diluting and boiling, the mass is filtered and evaporated until a drop removed on the end of a glass rod nearly solidifies when stirred on a watch glass. A little water is then sprayed on the surface and the whole submitted to fractional crystallization. The absorption spectrum soon shows that a rapid change is taking place. Small amounts of samarium and gadolinium are rapidly separated in the least soluble portion while the next fractions contain terbium and give oxides of a deep red-brown color. Dysprosium and holmium are more soluble than terbium. Yttrium places itself between holmium and erbium.[6]

[1] Demarcay, *Loc. cit.*

[2] *Compt. rend.*, 137, 792 and 138, 84.

[3] Urbain, *Compt. rend.*, 140, No. 9.

[4] The writer is applying the bromate method to a complicated mixture of samarium, gadolinium, terbium, dysprosium and holmium and is obtaining interesting results.

[5] James, THIS JOURNAL, 30, 182 and *Chem. News*, 97, 61.

[6] The writer, in a previous paper describing the serial order of the bromates, made an error in the position of yttriun. This element, as stated above, ranges itself in the fractions between holmium and erbium. The cause of the error was due to the fact that the material on which the serial order was worked out contained only a little yttrium and a fair amount of gadolinium. At the time, gadolinium was not suspected and the colorless bromate crystals were supposed to be due to yttria.

The most soluble portion contains erbium, thulium and ytterbium.

Terbium, Dysprosium and Holmium.—These elements are extremely difficult to separate. Operations with the bromates are still in progress. Terbium separates in the least soluble together with samarium and gadolinium. The separation of dysprosium from holmium is extremely slow and so much so that the bromate method is of no value for this work. Urbain recommends the fractionation of the double nickel nitrates from nitric acid of density 1.3 to separate samarium and gadolinium from terbium, dysprosium and holmium. The more soluble portion, consisting of terbium, etc., with some gadolinium, is converted into the simple nitrate and fractionally crystallized from concentrated nitric acid in the presence of bismuth nitrate. Terbium collects with the bismuth nitrate in the fractions between gadolinium and dysprosium. Fractional crystallization of the ethyl sulphates gives dysprosium. Small amounts only of dysprosium and terbium have been separated. The preparation of pure holmia has not yet been accomplished.

Yttrium.—Yttrium is obtained from the bromate fractions between holmium and erbium. Some fractions show holmium bands in addition to erbium. It is most easily prepared from the fractions that are free from holmium. The earths are precipitated from dilute boiling solutions of the bromates by the addition of boiling potassium hydroxide solution. The hydroxides are filtered off, washed and converted into the nitrates. Yttrium is then separated by the method of Muthmann and Rolig[1] as follows: The concentrated neutral nitrate solution is boiled and a thick cream of magnesium oxide added until the liquid no longer gives the absorption bands of erbium. The fractions that contain holmium in addition to erbium can be put through the same process. Yttrium oxide obtained by the bromate and magnesium oxide methods is snow-white and absolutely free from terbium, etc.

Erbium, Thulium, Ytterbium and Scandium.—These elements are separated from each other by the continued fractionation of the most soluble portion of the bromates. The erbium solutions become a beautiful rose tint. Thulium collects between erbium and ytterbium. The mother-liquor contains ytterbium with a very little scandium. The neutral solution is saturated with potassium sulphate when scandium potassium sulphate separates as it is insoluble in potassium sulphate solution. The filtrate on the addition of oxalic acid gives a precipitate of ytterbium oxalate.

The fractionation of the least basic earths is still being carried on with the object of preparing pure thulium for a determination of the atomic weight and also to confirm Urbain's lutecium.

In conclusion I again thank the Welsbach Company for large amounts

[1] *Ber.*, 31, 1718.

of material received through the courtesy of Dr. H. S. Miner. I also tender my thanks to the Christiania Minekompani, of Christiania, Norway, for many mineral specimens for examination.

NEW HAMPSHIRE COLLEGE, DURHAM, N. H.,
March 5, 1908.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE. NO. 2.]

ON VISCOSITY AND LUBRICATION.

BY CHARLES F. MABERY AND J. HOWARD MATHEWS.

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Excepting the work done in this laboratory during the last fifteen years in determining the composition of American petroleum, so far as we know, no attempts have been made to ascertain the composition of lubricating oils with reference to the hydrocarbons or even the series of hydrocarbons of which they consist.

Neither the composition of the oils nor the source of the petroleum from which the various products were manufactured have been relied on as a means of distinguishing differences in quality or durability, except a general distinction between straight hydrocarbon oils and compounded oils. Until comparatively recently, the refiner had to rely for high viscosity on mixtures of animal or vegetable oils with oils separated from petroleum, and the latter were obtained from Pennsylvania, Ohio, or other similar natural oils ordinarily referred to as paraffin oils, since they contained the solid paraffin hydrocarbons, C_nH_{2n+2}. Naturally, the refiner became convinced of the superiority of his compounded oils over straight hydrocarbon oils, and this idea has been maintained so persistently, it still prevails very generally with consumers of lubricating oils.

But within the last ten years, other varieties of petroleum have been found to yield lubricating oils with superior viscosity and wearing qualities which makes it no longer necessary to rely on compounded oils either for use on bearings or in cylinders. This is of especial importance with reference to cylinder oils, for it is well understood that the conditions of high temperatures and highly heated steam in cylinders lead to saponification of the animal or vegetable oil used in compounding, with consequent corrosion of the cylinder. As is well known, castor oil is one of the very best lubricating oils, especially for durability, but its general use is precluded by its high cost. It is now possible to prepare straight hydrocarbon oils fully equal in viscosity and wearing qualities to castor or any other high viscosity vegetable oil.

Viscosity is generally accepted as a standard of value in classifying lubricating oils, but it is not certain that it is reliable as indicating the durability and wearing qualities of oils differing widely in composition. There is little doubt that a confirmation of viscosity by chemical data

and frictional durability tests may be depended on to give accurate information for commercial use. The viscosity of lubricating oils has received much attention and several methods and forms of apparatus have been suggested for its determination, but for the most part of arbitrary construction and comparison, and differing so essentially that determinations made with different instruments are not easily and readily comparable. As thus determined, viscosity is but an arbitrary standard based on an assumption that the outflow of a liquid through an orifice, influenced as it is by several physical conditions, is a correct measure of surface viscosity between bearing surfaces. It is merely a relative comparison with an oil arbitrarily selected as a standard, or with water or by means of a metal apparatus arbitrarily constructed. But with the use of water, evidently, the conditions of temperature must be stated in the results, for the viscosity of water is quite different at different temperatures, and slight variations in temperature have likewise an important influence on the viscosity of oils.

It is, therefore, necessary to know the temperature coefficient of water, and it would be interesting to follow out a series of observations with an homologous series of hydrocarbons, although the possibility of such an investigation is almost precluded by the immense labor necessary in separating in an acceptably pure form the individual hydrocarbons. We have on hand, members of the different series C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-}, and we have made a series of observations on some of the individual hydrocarbons. Interesting results have also been obtained on the viscosity of mixtures, showing the influence of the hydrocarbons of the different series.

In attempting to arrive at a series of determinations which should avoid the errors in methods in which differences in specific gravity, and accurate observations of temperature are neglected, it was evidently inexpedient to use any of the commercial methods, especially since, as explained above, the data afforded by those methods are merely empirical, and with no definite relations to a common standard. The well-known method of Ostwald was selected, therefore, as best suited for these determinations, and the apparatus employed needs no detailed description. In this method a definite volume of liquid flows through a capillary tube under a definite head. In the calculation, the pressure under which the liquid flows through the capillary, is corrected for its density in the Ost ald formula:[1]

[1] Ostwald-I uther, Physico-Chemische Messungen., p. 20.

η = The viscosity of the liquid examined,
S = Density of the liquid examined;
t = Time of outflow of the liquid examined;
η_0 = The viscosity of the standard liquid;
S_0 = Density of the standard liquid;
t_0 = Time of outflow of standard liquid;
$\eta = \eta_0 St/S_0t_0$.

The values thus obtained, express the ratio of the viscosity of the liquid under examination to a standard liquid used for reference. Water is the standard liquid most commonly chosen, and the values of η are referred to as "Specific Viscosities," *i. e.*, the ratio of viscosity to that of water at that particular temperature. The advantage of using water consists in the ease with which it may be obtained sufficiently pure, and in the fact that the value in absolute units for the viscosity of water is the best known of any liquid, and specific viscosities may be converted easily into absolute units. The specific viscosities obtained at different temperatures are not comparable, since they express only the ratio at the particular temperature chosen and take no account of the change in volume of the apparatus, especially in the size of the capillary. To compare the results obtained at different temperatures, it is necessary to convert the values into absolute units, using the known values for the viscosity of water at the temperature used.

From interpolation and extrapolation of the result obtained by Thorpe and Rodger[1] we obtained the values $\eta = 0.01007$ at 20° C. and $\eta = 0.004625$ at 60° C., where η is the coefficient of viscosity in absolute units, *i. e.*, dynes per square centimeter. By multiplying the values obtained at 20° and 60° by these numbers, comparable results are obtained.

Constant temperature was maintained by placing the viscosimeter in a glass thermostat through which observations could be made, and which was supplied with water from a larger thermostat maintained at a constant temperature by means of an electric thermo-regulator. The water was pumped from the larger to the smaller thermostat by means of a small lift-pump operated by a hot air engine. The temperature in the glass thermostat was held at 20° (± 0.02); since the viscosity of the oils, like that of most liquids, changes about 2 per cent. per degree, this small fluctuation is negligible.

The measurements at 60°, were made in a glass thermostat of about 10 liters capacity in which the temperature was maintained by superheated steam injected at the bottom through a small orifice. The steam could be easily regulated and the temperature readily maintained at 60° (± 0.02). In observations on the paraffin hydrocarbons, it was found that viscosity increases with some regularity in the homologous series with decreasing percentages of hydrogen.

These hydrocarbons were obtained by long-continued fractional separations under systematic conditions, and their identity was shown by analysis and critical examination; but it is doubtful whether the homologues can be completely separated even by very prolonged distillation unless much larger amounts of material are used than is possible on a laboratory scale.

[1] *Proc. Roy. Soc.*, 1894; *Z. physik. Chem.*, 14, 361.

TABLE 1 (20°).

Hydrocarbon.	B. P.	Sp. gr.	Specific viscosity,
C_7H_{16}	98–100°	0.724	0.51
C_8H_{18}	125°	0.735	0.60
$C_{10}H_{22}$[1]	172–173°	0.747	0.96
$C_{10}H_{22}$	174–175°	0.753	0.95
$C_{10}H_{22}$	163°	0.745	0.89
$C_{12}H_{26}$[1]	209–210°	0.762	1.25
$C_{12}H_{26}$	212–214°	0.769	1.49
$C_{15}H_{32}$	158–159° (50 mm.)	0.793	2.79
$C_{15}H_{32}$[1]	155–158° "	0.796	2.75
$C_{16}H_{34}$	174–175° "	0.799	3.35
$C_{18}H_{38}$	199–200° "	0.813	5.97

In Table 1, it will be observed that viscosity increases somewhat irregularly with every increment of CH_2, and that the change is greater with the increase in molecular weight. Since the proportion of hydrogen to carbon apparently influences materially the value of viscosity, it seemed desirable to compare the viscosity of hydrocarbons of different series. In Table 2, are given the values for hydrocarbons with the same boiling points, but members of different series.

TABLE 2 (60°).

Series.	B. P.	Sp. gr.	Specific viscosity.
C_nH_{2n+2}	294–296° (50 mm.)	0.781	10.88
C_nH_{2n-2}	294–296° "	0.841	21.23
C_nH_{2n+2}	274–276° "	0.775	8.51
C_nH_{2n}	274–276° "	0.835	15.63

The greater viscosity of the hydrocarbons poorer in hydrogen, is clearly shown. In comparing the viscosities of the two hydrocarbons boiling at 294°–296° it will be observed that the difference is greater than the difference between the viscosities of the two hydrocarbons boiling at 274°–276°. This demonstrates the influence of a decreasing percentage of hydrogen since in the first set, the change is from $2n+2$ to $2n-2$, whereas in the second set, the change is only from $2n+2$ to $2n$. Both viscosity and specific gravity increase with the decreasing hydrogen. Another possible influence must not be overlooked, however, namely, the internal structure of the different hydrocarbons. It is reasonable to assume that the straight or open-chain structure of the paraffin hydrocarbon C_nH_{2n+2} behaves differently under the stress of internal forces on which viscosity depends, from the ring or cylic structure, which must be accepted for the other series, until more is definitely known concerning their constitution. Certainly this is plainly shown in lubrication, where the paraffin hydrocarbons are of comparatively little value.

If, then, the lower series furnish lubricators with greater viscosity, the addition of a member of a higher series should give a mixture lower in

[1] Of approximately this composition.

viscosity. Observations were therefore made on mixtures of pure hydrocarbons of the different series with reference to variations of viscosity, and the results of these measurements are given in Tables 3 and 4.

TABLE 3 (20°).

INFLUENCE OF A SOLID PARAFFIN HYDROCARBON.

Hydrocarbon.	B.P.	Sp. Gr.	Specific viscosity.
(*a*) Penn. distillate C_nH_{2n-2} filtered.....	312–314° (50 mm.)	0.868	87.42
(*b*) Same cooled to —10° and filtered.....	312–314° "	0.868	88.16
(*c*) *b* + 2.35 per cent. solid paraffin C_nH_{2n+2} of same B. P.....	312–314° "	0.868	82.30
(*d*) Penn. distillate C_nH_{2n} cooled to —10° and filtered.....	276–278° "	0.861	37.57
(*e*) *d* + 2.5 per cent. solid paraffin hydrocarbon C_nH_{2n+2} of same B. P.....	276–278° "	0.860	36.39

The amounts of solid paraffin hydrocarbons added in these experiments were all that the oils could hold in solution at that temperature. Although no appreciable changes appear in specific gravity, there were material changes in viscosity. Table 4 shows that the diminution in viscosity still holds at a higher temperature, but in a less marked degree even when a larger portion of the paraffin hydrocarbon is introduced.

TABLE 4 (60°).

INFLUENCE OF A SOLID PARAFFIN HYDROCARBON.

Hydrocarbon.	B. P.	Sp. Gr.	Specific viscosity.
(*a*) C_nH_{2n-2}.....	294–296° (50 mm.)	0.841	21.23
(*b*) C_nH_{2n+2}.....	294–296° "	0.781	10.88
(*c*) Pa. hydrocarbon C_nH_{2n}.....	274–276° "	0.838	15.63
(*d*) Pa. hydrocarbon C_nH_{2n+2}.....	274–276° "	0.775	8.51
(*e*) *c* + 5 per cent. of *d*.....	....	0.831	15.16

South American Oils.

Two well-fractioned distillates from South American petroleum of undetermined series, but doubtless poor in hydrogen, were examined at 20° with the following results:

TABLE 5.

	B. P.	Sp. gr.	Specific viscosity.
Distillate 1.....	155–160° (50 mm.)	0.884	8.14
Distillate 2.....	215–220° "	0.896	19.57

So far as viscosity is an indication of lubricating value, it is evident that these distillates are inferior to the Pennsylvania distillates of the same gravity. The heaviest Pennsylvania distillate examined, with lower gravity than the South American distillates, *viz.* 0.08687, had a viscosity of 88.16 as compared with the numbers 8.14 and 19.57 for the latter. But on the other hand if we consider the properties of distillates taken at the same temperatures, the South American distillates have a much greater

gravity and viscosity. It is evident therefore that neither gravity nor boiling point can be depended on for lubricating value unless the source of the oil is known. The method of manufacture has also much to do with relation of specific gravity and lubricating value.

Valuation of Lubricating Oils.

The various standards which have been proposed for the valuation of lubricating oils, are based on their physical properties, especially on specific gravity and viscosity. Both specific gravity and viscosity are, however, unreliable, unless the source and composition of the oil are known, and unless viscosity is still further defined by frictional tests on bearings under definite conditions which demonstrate the wearing quality of the oil. As is well known, many lighter oils have a greater viscosity than other heavier oils. With these limitations, the property of viscosity has a direct relation to lubricating value.

An ideal lubricator is evidently one which holds two bearing surfaces at a sufficient distance from each other to prevent friction between them and at the same time has the least possible amount of internal friction so that the work necessary to overcome the friction of the oil particles upon each other may be reduced to a minimum. If the oil has too great an internal friction, considerable mechanical energy is expended in overcoming this friction and in conversion of mechanical energy into heat, which should be avoided as far as possible. The choice of a lubricator must, therefore, depend upon the weight to be supported and upon the speed desired. At a high speed, an oil of small internal friction should be chosen, but for slow heavy work, an oil of greater viscosity must be used to support the weight, and because of the slow speed, the greater internal friction of the oil is of less consequence. The viscosity of an oil then, with a knowledge of its composition and with the aid of frictional tests, gives a direct measure of its usefulness as a lubricator under any given conditions, since viscosity is merely another term for internal friction.

But viscosity measured at ordinary temperatures may lead to erroneous conclusions concerning true lubricating value for higher temperatures. This would be especially true for light loads and high speeds where the temperature is considerably higher than the surrounding temperature. The viscosity of all liquids decreases with rise of temperature, but not to the same extent for all liquids. In general, the decrease is about 2 per cent per degree centigrade, within ordinary ranges of temperature. The following table shows the dependence of viscosity on temperature for two Pennsylvania distillates.

TABLE 5.

Hydrocarbon.	B. P.	Viscosity in dynes per sq. cm. at 20°.	Viscosity in dynes per sq. cm. at 60°.	Change in viscosity per degrees C.
C_nH_{2n-2}	312–314° (50 mm.)	0.8803	0.1320	2.12%
C_nH_{2n}	276–278° (50 mm.)	0.3783	0.0723	2.02%

The first oil shows a greater variation per degree than the latter of the C_nH_{2n} series. The coefficient of the more mobile C_nH_{2n+2} distillate with the same boiling point at temperatures above its melting point, should be still smaller. Small differences in the temperature coefficient of viscosity should also be expected in the same series when members of different boiling points are compared. It may readily occur then that two oils have quite different viscosities at high temperatures while at lower temperatures the value should be the same.

The viscosity of a hydrocarbon oil may be changed, as is commonly done, by the addition of viscous vegetable oils such as castor. Such blended oils, made to meet specifications for a required viscosity, are in common use. For certain kinds of work, such oils are doubtless serviceable, but probably have less durability than mineral oils of equivalent viscosity. In cylinders where the oil comes in contact with superheated steam, the vegetable constituents must be saponified to a greater or lesser extent, with consequent danger of corrosive action by the free acid. There is in fact at present, less necessity for the use of compounded oils to obtain desirable viscosity and wearing qualities since the recent development of oil territory which yields heavy products.

Durability tests on compounded oils and pure distillates by a frictional machine in the Case mechanical laboratory have shown the superior frictional qualities of the mineral oils.

Allusion has been made to the fact that viscosity alone cannot always be relied on to give a correct estimate of the wearing qualities of a lubricating oil on a bearing. Much time has been devoted to the wearing qualities of oils in this laboratory, and some of the results were presented in a paper at the New York meeting of the American Chemical Society, December, 1906. The machine employed in these tests was constructed by Prof. C. H. Benjamin for the mechanical laboratory of Case School of Applied Science. It consists of a bearing in two sections so arranged that the upper section can be raised, and when in position can be weighted by means of strong springs on the axle to be lubricated. Attached to the upper section of the bearing is a lever arm extending outward over the platform of a scale, and the outer end rests on a support standing upright on the scale platform by which the scale registers by changes in weight the varying pressure caused by changes in friction. An oil cup is connected with the bearing in such a manner that a regular supply of the oil to be tested is permitted to flow over the journal. A thermometer is also inserted in the bearing close to the journal for the purpose of indicating the changes in temperature during a test. An examination of a lubricating oil by this method, consists in allowing the oil to run on the axle at the rate

of six to eight drops per minute for two hours, noting the temperature and pressure on the balance every five minutes. At the end of this period the flow of oil is stopped and the journal allowed to run until the oil ceases to lubricate, which is immediately shown by greatly increased frictional pressure and a large rise in temperature. The crucial test of the oil is the time it can support the axle after the flow is stopped.

The number of revolutions was set at about 500 per minute, and an occasional reading of the speed was taken to be sure that the axle was revolving under fairly constant conditions. The pressure on the axle exerted by the spring set on the upper half of the bearing was equivalent to 1300 pounds. In practice, evidently every oil should be tested under an equivalent of the load and speed it is expected to carry. The results of several of the oils tested are given below. Every oil was run for two hours with continuous lubrication, and the time stated in the table is reckoned from the end of the hour when the flow was stopped, to the time when the oil refused to lubricate, which was indicated by sudden and large increase in temperature and frictional load. Such a durability test affords a fair comparison of the ability of the oil to support friction.

Having on hand a variety of hydrocarbons of the series C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2} and C_nH_{2n-4} which have accumulated during the years one of us has been occupied in ascertaining the composition of American petroleum, an opportunity was afforded to ascertain by frictional tests whether hydrocarbons of a different series exhibit differences in wearing capacity corresponding to variations in viscosity. For the purpose of comparing the frictional qualities of these hydrocarbons with the requirements of lubricators in actual use, several vegetable oils were included, *viz.*, castor, sperm, and rape oils, which are the best lubricators of their class, and often used in compounding with petroleum oils as an aid to the viscosity of the latter. Some results of the best compounded oils are also included for comparison. The following elements were used in the calculation of results:

Constant of lever arm (determined by independent observations)	13.656 lbs.
Radius of lever arm	31.625 inches.
Radius of journal	1.61 "
Load	1,300 pounds.

$$\text{Formula: Coefficient of friction} = \frac{\text{Scale reading} - 13.625\ \frac{31.625}{1.61}}{1300}.$$

The real tests of lubricating capacity depend on temperature, measure of friction, and the time the oil continues to lubricate after it ceases to flow on the journal. The latter observations are given in the column headed "Test of durability." It is interesting to observe that the life

TABLE 6.

Oil treated.	B. P.	Specific gravity.	Specific viscosity 20°.	Test of durability. Minutes.	Temperature. Start.	Temperature. 2 hrs.	Temperature. Break.	Coef. of friction. Start.	Coef. of friction. 2 hrs.	Coef. of friction. Break.
Hydrocarbon C_nH_{2n}	274–276° (50 mm.)	0.861	37.57	120	76°	107°	124°	0.02	0.01	0.015
Hydrocarbon C_nH_{2n-2}	312–314° (50 mm.)	0.868	88 16	150	80°	130°	185°	0.01	0.02	0.02
Hydrocarbon C_nH_{2n-x}	228–230° (30 mm.)	0.923	94.3	210	75°	113°	164°	0.03	0.01	0.01
			Viscosity.							
Castor		0.97	104(210°)	150	70°	165°	225°	0.04	0.025	0.03
Sperm		0.94	192(90°)	140	70°	120°	160°	0.02	0.01	0.01
Rape		0.91	108(150°)	120	80°	160°	230°	0.03	0.02	0.05
Cylinder oil (compounded)		0.92	123(212°)	75	80°	180°	210°	0.05	0.03	0.06
Cylinder oil (compounded)		0.89	135(210°)	200	80°	185°	225°	0.07	0.03	0.06

of the individual hydrocarbons increases with the decrease in hydrogen, and in a similar ratio to the increase in specific viscosity. Doubtless the most valuable quality of an oil is its ability to reduce friction to the smallest value; of the hydrocarbons compared in this test, the one with least hydrogen, of the series C_nH_{2n-4} seems to show the best efficiency, as it also shows the greatest durability. Of the vegetable oils compared, the castor shows the longest life, but the sperm shows the least coefficient of friction, as it does also the lowest temperatures. The hydrocarbon C_nH_{2n-4} stands ahead of the vegetable oils in durability, and the equal of the sperm in temperatures and coefficient of friction. In the above table, temperatures are selected at the beginning of the test, at the end of two hours, and when the oil ceases to lubricate. The coefficient of friction is also calculated at these points. This method appears to be capable of giving valuable information concerning the nature of lubricating oils. Like all tests of such oils, the results are relative referring to some common standards. Evidently in practice, these standards must be based on the work required of the oil, taking into account certain data, such as speed of th e journal and the load carried. The coefficient of friction as used above represents the fraction of one pound for each pound of load on the journal which is sustained by the oil in use.

With reference to the comparative value of the various series of hydrocarbons in petroleum from which lubricating oils are prepared, it must be understood that the series C_nH_{2n+2} has a low lubricating value; this was shown above in tests of specific viscosity. Lubricating oils prepared from Pennsylvania petroleum consist for the larger part of the series C_nH_{2n} and series C_nH_{2n-2}. Those from the heavier oils consist largely of the series C_nH_{2n-2} and the series C_nH_{2n-4}.

As to the structural constitution of the series of hydrocarbons in lubricating oils, at present nothing whatever is known. The series C_nH_{2n+2} is doubtless represented by the straight chain or its isomers, all with the open chain. The series poorer in hydrogen, no doubt have the cyclic ring structure of the form of condensed benzene rings in part, or condensed methylene rings, single larger rings than are at present recognized, or smaller rings with condensed side chains.

CLEVELAND, OHIO.

THE COLORED SALTS OF SCHIFF'S BASES.

II. THE HYDROCHLORIDES OF BASES FORMED BY CONDENSING *p*-AMINODIPHENYLAMINE WITH AROMATIC ALDEHYDES.

BY F. J. MOORE AND R. G. WOODBRIDGE, JR.

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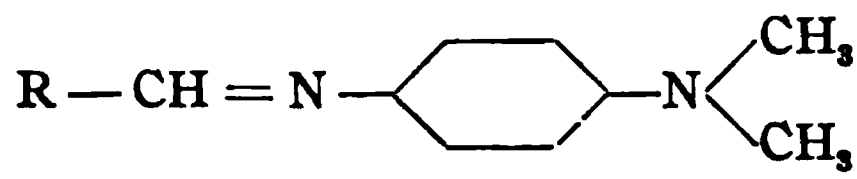
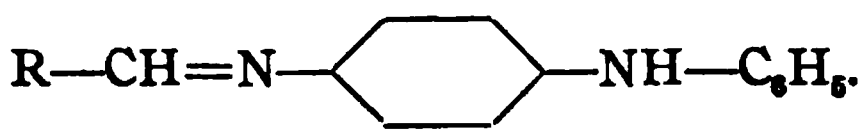
In a paper recently published by one of us, in collaboration with Mr. R. D. Gale,[1] attention was called to the fact that bases of the general formula

[1] THIS JOURNAL, 30, 394 (1908).



add successively two molecules of hydrochloric acid to form salts which differ markedly in color. While the bases themselves are, for the most part, of a light yellow or orange color, the salts containing one molecule of acid are dark red, while those containing two molecules are light or pale yellow, resembling the free bases in this respect.

The present investigation was undertaken in order to determine whether the behavior described was not still more general, and for this purpose, to study the color of the salts of bases formed by condensing *p*-aminodiphenylamine with aromatic aldehydes. These condensation products have the general formula



In the paper above referred to by Moore and Gale, a preliminary statement was made to the effect that these bases add one molecule of hydrochloric acid to form dark red salts, but that they do not add a second molecule of the acid. This statement requires modification. The behavior of these diphenyl compounds is, in fact, entirely analogous to that of the dimethyl compounds already described. In this case, however, the dihydrochlorides are formed with more difficulty. If one molecule of the base be treated in ethereal solution with two molecules of dry hydrochloric acid dissolved in ether, the resulting precipitate is dark colored, consisting of the monohydrochloride. If, now, the solution be kept saturated with hydrochloric acid by passing a current through it for several hours, the precipitate first formed gradually becomes lighter in color, and in some cases, practically white. When this precipitate is analyzed, it is found to contain two molecules of acid. Of the dihydrochlorides studied, all but one are sufficiently stable to retain the two molecules of hydrochloric acid when dried in a vacuum desiccator containing caustic soda. The exception is the salt of the base formed by condensing *p*-aminodiphenylamine with cinnamic aldehyde. This salt is quite light in color when first prepared, but after standing some days in the desiccator, it becomes dark, and as the analytical data clearly show, gradually loses a whole molecule of acid.

It is true of all the dihydrochlorides that their color becomes much darker on standing, even in dry air, and some of them become quite deep red again. We are at some loss to account for this. It may be due to the fact that there are two dihydrochlorides, one red and the other yellow. Another explanation would be that some acid had been lost, resulting in the formation of sufficient monohydrochloride to account for the color observed. Inspection of the analytical data presented below will show

that any such loss is too small to clearly show itself in the analyses. This, however, is not conclusive, as we know, for example, that a very extensive blackening of silver chloride has very little influence upon its composition, and thus, in this case also, the presence of a small amount of the salt containing only one molecule of acid might account for the phenomenon. The behavior of the cinnamic aldehyde compound above referred to, would certainly point, by analogy, to a loss of acid as the cause of the change in color. If two kinds of salts are present, whatever their nature, it may prove possible, by means of solvents, to isolate one or both of them, and some experiments in this direction are in progress.

Experimental Part.

The *p*-aminodiphenylamine used in this investigation was prepared from diphenylamine by treatment with nitrous acid, forming the nitrosamine. The latter was then subjected to the Fischer-Hepp rearrangement, forming the *para* nitroso compound, and this was finally reduced with ammonium sulphide. So prepared, the substance forms almost colorless needles of a pearly luster melting at 75°.

Benzylidene p-aminodiphenylamine.—This compound was first prepared by Heucke[1] by the action of *p*-aminodiphenylamine upon benzaldehyde. The base is of a pale yellow color.

The monohydrochloride is blood-red. Calculated for $C_{19}H_{16}N_2,HCl$; Cl, 11.43; found, 13.48.

The saturated salt, prepared by subjecting the ethereal solution to the action of hydrochloric acid gas for some hours, is nearly white when first precipitated. When kept in a desiccator over caustic soda it turns reddish. The analysis speaks, however, for the presence of two molecules of acid in the salt. Calculated for $C_{19}H_{16}N_2,2HCl$: Cl, 20.53; found, 19.95 and 19.90.

Salicylidene p-aminodiphenylamine.—This compound was also prepared by Heucke. The base is light yellow.

The red hydrochloride has the following composition: Calculated for $C_{19}H_{16}ON_2,HCl$: Cl, 10.91; found, 11.21.

The dihydrochloride is light yellow. Calculated for $C_{19}H_{16}ON_2,2HCl$: Cl, 19.63; found, 20.59.

Piperonylidene p-aminodiphenylamine.—The base is of a light yellow color and melts at 116°.

Red hydrochloride. Calculated for $C_{20}H_{16}O_2N_2,HCl$: Cl, 10 07; found, 10.24.

The saturated salt is light yellow. Calculated for $C_{20}H_{16}O_2N_2.2HCl$: Cl, 18.22; found, 18.49.

[1] *Ann.*, **255**, 189 (1889).

Anisylidene p-aminodiphenylamine.—This substance crystallizes from alcohol in silver-gray scales of a pearly luster which melt at 105°. Its composition was confirmed by a nitrogen determination. Calculated for $C_{20}H_{18}ON_2$: N, 9.30; found, 9.48.

The monohydrochloride is red, but of a lighter shade than most of the others hitherto examined. Calculated for $C_{21}H_{16}ON_2,HCl$: Cl, 10.47; found, 12.42.

The dihydrochloride as we obtained it, was of a pale pink color. Calculated for $C_{20}H_{18}ON_2,2HCl$: Cl, 18.90; found, 19.57 and 19.75. Although these results are a little high, we should hardly be justified in ascribing this to a tendency to add three molecules of acid as does anisylidene *p*-aminodimethylaniline.

Cinnamylidene p-aminodiphenylamine.—This compound was prepared by condensing *p*-aminodiphenylamine with cinnamic aldehyde. The base crystallizes from alcohol in brilliant yellow scales and melts at 145°. Its composition was checked by a nitrogen determination. Calculated for $C_{20}H_{18}N_2$: N, 9.42; found, 9.37.

When an ethereal solution of this base is treated with dry hydrochloric acid, the resulting precipitate is extremely dark in color, almost black. Calculated for $C_{20}H_{18}N_2,HCl$: Cl, 10.59; found, 10.55.

An excess of hydrochloric acid finally yields a product of much lighter color, which, when first filtered off, is pale pink. This substance, however, when dried in a vacuum desiccator over sulphuric acid and caustic soda, rapidly turns dark. A sample of this product, after standing in the desiccator for two days, still retained a perceptible odor of hydrochloric acid and contained 16.14 per cent. of chlorine. A dihydrochloride should contain 19.10 per cent. The same material, after standing for five days, was nearly black, and no odor of hydrochloric acid was noticeable. This material contained 11.06 per cent. of chlorine, which is only slightly in excess of that required for a monohydrochloride, as indicated above.

Summary.

When *p*-aminodiphenylamine is condensed with aromatic aldehydes, the resulting bases show the same curious color phenomena in the formation of their salts which are exhibited by the analogous compounds of *p*-aminodimethylaniline; that is, they unite with one molecule of acid to form dark colored salts and with two molecules to form light colored ones. The salts containing two molecules of acid are less easily formed than in the cases hitherto studied, and, in a single instance, the second molecule of acid is readily lost.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
BOSTON, April 7, 1908.

THE ENDO- AND EKTOINVERTASE OF THE DATE.[1]

By A. E. Vinson.

Received April 1, 1908.

In a recent paper the writer[2] called attention to the fact that the invertase of the date could not be extracted from the active tissues by solvents until the fruit ripened. In other words the invertase changes suddenly from an endo to an ektoenzyme.[3] The invertase of the green date thus corresponds very closely, in its behavior towards solvents, to the invertase of certain yeasts,[4] of immature *Penicillium*,[5] of *Monilia candida*,[6] and of various parts of growing plants,[7] notably the rootlets of seedlings; to the urease in the torula causing alkaline fermentation of urine;[8] to Buchner's[9] zymase of beer yeast; and finally to several zymogens, notably that of diastase which occurs in the scutellum of ungerminated grain[10] and which hydrolyzes soluble starch only, the diastase of translocation of Brown and Morris.[11] It probably corresponds also to the zymogen or proferment of the proteolytic enzymes observed by Vines[12] in yeast, beans, and other plant tissues, and possibly mistaken by him for vegetable ereptase. After presenting the general facts relating to the insoluble invertase of the green date the application of a new hypothesis will be made which seems to harmonize these various phenomena without assuming differences in permeability of the cell wall.

The action of green date tissue in inverting cane sugar, while no active extract can be prepared, might be considered as due to the living cells, under the influence of cane sugar, secreting invertase[13] or activating some

[1] Read at the Chicago meeting of the American Chemical Society.

[2] *Bot. Gaz.*, **43**, 393 (1907).

[3] M. Hahn, *Z. Biol.*, **40**, 172; see also Green, Soluble Ferments, Cambridge, 1899, p. 116; Oppenheimer, Die Fermente, Leipzig, 1903, p. 72.

[4] Beer yeast, O'Sullivan and Tompson, *J. Chem. Soc.*, **57**, 873 (1890); **61**, 593 (1892); Fernbach, Thesis, Paris, 1890, through Pottevin and Napias; Pottevin and Napias, *Compt. rend. soc. biol.*, **50**, 237; Milk sugar yeast, lactase, E. Fischer, *Ber.*, **27**, 3481, 1894, etc.

[5] *Penicilium glaucum*, Bourquelot 1886, through Green, p. 115; *P. duclauxi*, *Bull. soc. mycol.*, **8**, 147 (1891).

[6] Hansen, through Fischer and Lindner; E. Fischer and Lindner, *Ber.*, **28**, 3034 (1895); Buchner and Meisenheimer, *Z. physiol. Chem.*, **40**, 167; Fischer, *Z. physiol. Chem.*, **26**, 77 (1898).

[7] Brown and Morris, *J. Chem. Soc.*, **1893**, 633; Brown and Heron, *Proc. Roy. Soc.*, **1880**, 393; J. O'Sullivan, *J. Chem. Soc. Proc.*, **16**, 61; *Abst. Centb.*, **1900**, 773; *J. Chem. Soc.*, **77**, 691, 1900.

[8] Sheridan Lea, *J. Physiol.*, **1885**, 136.

[9] *Ber.*, **30**, 117, 1110, 2668; **31**, 209, 568, 1084, 1090, 1531; **32**, 127.

[10] Reed, *Ann. of Bot.*, **1904**, 267.

[11] *J. Chem. Soc.*, **1890**, 458; Vines, *Ann. of Bot.*, **1891**, 409.

[12] *Ann. of Bot.*, **16**, 10; **17**, 237, 597; **18**, 289; **19**, 149; **20**, 113.

[13] Effront, p. 69–70.

zymogen, either soluble or insoluble, already existing in the cell; that is, the inversion was due to some activity of the living protoplasm.[1] This point, however, was readily answered in the negative by a short series of tests in the presence of ordinary killing reagents. The inversion curves for equal weights of green and of ripe date pulp were determined and found to be practically identical. Similar amounts of green and of ripe pulp from the same sample as was used for the blank, were allowed to act upon equal quantities of cane sugar under the same conditions, excepting that 1 per cent. of chromic acid, $^1/_2$ per cent. of picric acid and 2 per cent. of formaldehyde were added to the respective samples. If the inversion by the green date were due to living protoplasm, its inverting power would be inhibited to a much greater degree than that of the ripe date, where the invertase is known to exist in its soluble form. In all cases there was considerable inhibition, but the curves for both green and ripe pulp were approximately parallel and of the same order. These results were fully confirmed by later experiments, designed to break down the resistance of the plasmotic membrane, by treating the green pulp with chloroform, ether, toluene, and other reagents. These killed the protoplasm but left the inverting power of the tissues unaffected. The inverting action of chromic acid under the same conditions was determined. The following abridged table shows the effect in a general way of these protoplasmic poisons on the rate of inversion.

[1] NOTE.—Whatever our personal beliefs concerning the mechanism of biochemical processes may be, it is not always an easy matter to differentiate clearly between enzymatic and protoplasmic agencies. This is abundantly exemplified in the literature; thus Hugo Fischer (*Cent. Bakt.*, 1903, 453) says:

"Unrichtig ist es aber darum auch, enzymatische Vorgänge nun als 'rein chemische' grundsätlzich von denen zu trennen, die man nicht in zellenfreier Lösung sich abspielen lassen kann; die Eiweissynthese ist gerade so gut ein chemischen Vorgang wie die alkoholische Garüng. Denn, dass das Agens der letzteren sich in Wasser löst, das der ersteren nicht, ist zwar für die Laboratoriumstechnik wesentlich, viel weniger aber für die theoretische Physiologie." Bokorny (*Pflüger's Arch.*, 90, Heft 11–12, autoabst. *Centb. Bakt.*) "Die wirkliche Entscheidung über Protoplasma oder Enzymnatur konnte hier wie immer nur durch den Nachweis der bestimmten Organization oder des Fehlens einer solchen hierbei geführt werden. * * * * Die Löslichkeit in Wasser spricht gegen die Protoplasmanatur, da das Protoplasma nach den bisherigen Beobachtungen nie ein wirkliche Lösung darzustellen scheint. Doch ist auch bei einer Lösung, wenn dieselbe eine, "micellare" ist, Organization, das ist bestimmte specifische aneinanderreihung der Molecüle möglich." M. Hahn (*Ber.*, 31, 200) quotes Neumeister (*Lehrb. d. physiol. Chem.*, 137): "Für die tierischen Zellen nimmt Neumeister an dass die cellulare Verdauung ohne Enzyme lediglich durch eine eigenartige Thätigkeit des lebenden Protoplasma zu Stande kommt." Wills (Review of Buchner's book, Die Zymasegärung, *Centb. Bakt.*, 1903, 464): "Die Tatsache, dass die beiden Erscheinungen augenscheinlich durch dieselben Momente beinflusst werden, legt den Gedanken nahe, dass auch die Reduktionswirkung auf der Wirkung enzymatige Körper beruht, der für gewöhnlich in der Leibessubstanz der zellen eingeschlossen ist."

EFFECT OF PROTOPLASMIC POISONS ON THE RATE OF INVERSION OF CANE SUGAR BY GREEN AND BY RIPE DATE TISSUES.

	No poison.		Chromic acid.			Picric acid.		Formaldehyde.*	
Time.	Ripe.	Green.	Ripe.	Green.	Alone.	Ripe.	Green.	Ripe.	Green.
Nov. 27	+4.81	+6.02	+4.81	+5.41	+4.75	+4.72	+6.43	+4.65	+5.73
Nov. 28	+2.65	+1.63	+2.59	+1.09	+4.61	+5.12	+5.83	—0.06	+0.93
Nov. 29	+0.10	—0.56	+1.03	+0.07	+4.20	+3.61	+5.08	—1.00	—0.67
Nov. 30	—1.76	—1.81	—0.66	—0.85	+4.04	+3.32	+4.67	—1.81	—1.36
Dec. 1	—2.32	—2.25	—1.93	..	+3.95	+2.93	+4.23	—2.10	—1.99
Dec. 3	—2.07	—2.24	—1.10	—0.98	+4.14	+1.91	+2.81	—2.01	—1.92
Dec. 12	—2.45	—2.44	—1.32	—1.95	+4.13	—1.29	—0.85	—2.05	—1.99
Dec. 22	..	..	..	..	..	—2.04	—1.95	..	..

Since the invertase becomes soluble at the time of ripening and the tannin becomes insoluble at the same period, it would appear entirely possible that, on crushing the green fruit, the soluble tannin, which is confined to specific cells, would precipitate the invertase and prevent its extraction. It has been shown by Brown and Morris[1] that a decoction of hops will not extract diastase from malt until after the tannin has been removed by treatment with hide powder. They find also that the diastase of the hop strobile cannot be extracted with water and that those plants whose aqueous extracts show weak diastatic powers are rich in tannin.[2] This is especially true of *Hydrocharis*.[3] Warcolier[4] belives the presence of abnormal quantities of starch in bruised apples to be due to the action of escaped tannin on the diastase. These considerations led the writer to investigate the relations between tannin and invertase in general, and especially the possibility of the phenomenon of insoluble invertase in the green date being due to soluble tannin. I have not been able to connect the tannin with enzymic action, although its disappearance at the time the invertase becomes soluble and its presence in those parts of plants where metabolism is rapid, as in the tips of shoots like those of the rose, seem to be suggestive.

The first point to determine is whether tannin in relatively large amounts is in any way inimical to the action of invertase. The effect of added tannin was studied both with date pulp and date extract. Twenty grams of ground date were disintegrated with 100 cc. of water, varying amounts of tannin added, then 500 cc. of sugar solution. The values in the following tables are the readings given on the sugar scale of the saccharimeter, when double the normal weight of the sugar solution was used. The variations in initial reading are due to inversion before weighing off the quantities for polarization.

[1] *Trans. Inst. of Brewing*, 6, 94 (1893).
[2] *J. Chem. Soc.*, 63, 604, 640.
[3] *Ibid.*, 653.
[4] *Compt. rend.*, 141, 405 (1905).

EFFECT OF TANNIN ON RATE OF INVERSION OF CANE SUGAR BY DATE TISSUE.

	No tannin.	0.25 gram.	0.50 gram.	0.75 gram.	1 gram.
Initial reading.....	+14.5	+14.2	+12.8	+13.2	+13.0
24 hours later.....	— 4.0	— 4.0	— 4.7	— 4.7	— 4.9

The presence of added tannin seems to slightly increase the rate of inversion rather than retard it.

The extracts used in the following table were made from 250 grams of ground date with 400 cc. of water and with 200 cc. of water and 200 cc. of glycerol respectively. In the experiments 500 cc. of sugar solution were treated with 50 cc. of date extract.

EFFECT OF TANNIN ON THE RATE OF INVERSION OF CANE SUGAR BY DATE EXTRACT.

	Water extract.		Glycerol extract.	
	No tannin.	1 gm. tannin.	No tannin.	1 gm. tannin.
Initial reading.....	+14.9	+14.2	+15.2	+14.3
24 hours later.....	— 5.2	— 5.5	— 5.0	— 6.0

The effect of tannin on the solubility of the enzyme, however, is a very different matter, as shown by the references cited above. A short series of experiments was planned to study this effect on the solubility of date invertase in both water and glycerol. 250 grams of ground date (Amari and Amhat mixed, one year old) were treated with 400 cc. of water, with and without the addition of 5.0 grams of tannin, and also with 200 cc. each of water and glycerol with and without tannin. 50 cc. of each of the extracts were then added to 500 cc. of sugar solution and the rate of inversion determined as before.

EFFECT OF TANNIN ON THE SOLUBILITY OF DATE INVERTASE IN WATER AND GLYCEROL AS DETERMINED BY THE RATE OF INVERSION.

	Water alone.		Water + glycerol.	
Date.	Without tannin.	With tannin.	Without tannin.	With tannin.
June 21.....	+14.85	+15.8	+15.2	+15 2
June 22.....	— 5.2	+14.6	— 5.0	— 1.3
June 25.....	— 5.6	+ 9.5	— 5.1	— 5.5

The press residues appeared about as active as the original ground date. The glycerol solution, being somewhat turbid, was allowed to settle several days, the clear upper portion decanted off, and the solid residue separated and washed in a small centrifugal. 50 cc. of the clear upper portion gave a result almost identical with that obtained from 50 cc. of the unsettled solution. The solid residue from the entire extract showed only a weak inverting action.

This solubility of the tannin enzyme compound in glycerol, as compared with its behavior toward water alone, seemed so unusual that I thought it desirable to change the conditions somewhat. Accordingly two samples, each containing 250 grams of the same date material and 5 grams of added tannin, were treated with 200 cc. of water, the one receiving 200 cc. of

glycerol at once and the other receiving a similar quantity two days later. Both were macerated 24 hours longer, pressed, and the turbid extracts allowed to stand in long narrow tubes for two weeks. The sample which had stood two days with the tannin before the glycerol was added, settled out clear in a few hours; but the other, which received the glycerol at once, remained slightly cloudy, tending rather toward opalescence. Considerable residue had separated out in both cases, from which the supernatant solution was carefully siphoned. These solutions were then tested as before, using 50 cc. of both the clear upper portion and the turbid lower portion.

EFFECT OF THE TIME OF ADDING GLYCEROL ON THE SOLUBILITY OF DATE INVERTASE IN THE PRESENCE OF TANNIN.

	Glycerol added at once.		Glycerol added after two days.	
Date.	Upper portion.	Lower portion.	Upper portion.	Lower portion.
July 16	+15.2	+14.3	+15.9	+15.7
July 17	— 5.6	— 5.6	+11.1	+ 4.5
July 18	— 5.65	— 6.0	+ 6.7	— 2.7
July 19	...	....	+ 3.7	— 4.3
July 24	...	....	— 5.0	— 6.0

These results indicate a marked solubility of the tannin-invertase compound in glycerol, especially when the glycerol was added at once. If the inversion had been due to a suspended insoluble invertase compound the first two columns of the table would show a marked difference, such as is apparent in the case where glycerol was added later. From these observations, we may conclude that if green date contained any soluble invertase its extraction would not be seriously hindered by the tannin liberated when the fruit was crushed, provided the glycerol was added at once. Numerous samples of green dates from several different invert-sugar varieties, treated in this way, have given negative results, although the press residues themselves were always very active, even after prolonged washing with water. While this test in itself should suffice to demonstrate that the invertase of the green date is not prevented from going into solution by the soluble tannin present, the distribution of the tannin in the fruit is such that it can be dissected away readily and leave a considerable mass of tannin-free tissue. For this purpose one of the larger varieties, such as Rhars or Amraayah, serves best. The tannin in the ovulary of the date exists during all stages of its growth in a layer of large tannin cells just beneath the skin and easily visible to the naked eye, so that it can be pared away as readily as the peel of any other fruit. After removing the seed, the fibrous envelope, which also contains tannin, is easily scraped out. By carefully comparing the inverting power of equal weights of pulp from the outer tannin-bearing and the inner tannin-free portions of the same sample, no appreciable difference could be detected. Extracts of the two portions were invariably inactive. This shows, beyond doubt, that the insolubility of the

invertase in the green date is not the result of the presence of soluble tannin, and the change in the solubility of the invertase and the disappearance of soluble tannin are not directly connected, although they coincide very closely in time.

It remains yet to show whether green date tissue, in the act of inverting cane sugar, does or does not secrete invertase into the surrounding medium as some yeasts are known to do, or whether a pre-existing soluble proinvertase, a zymogen, such as Pantanelli[1] has lately shown to exist in *Mucor*, was rendered active. To disprove this, portions of tannin-bearing and of tannin-free date tissue were allowed to act on cane sugar solution several hours. After the sugar was inverted, the juice was pressed off and more cane sugar added to the extract, but no further inversion took place even after standing several days. Thus no appreciable quantity of invertase passes from the green date into the surrounding medium during the process of inversion; the inversion must take place within the cell.

This brings us face to face with the long-accepted theory governing all these cases; namely, that it is a matter of the impermeability of the cell wall to the enzyme. This theory was first advanced in 1871 by Hoppe-Seyler,[2] who had observed that the invertase could be extracted from yeast cells after treating them with alcohol, the assumption being that such treatment broke down the resistance of the protoplasm to the passage of the enzyme. This same theory has worked well in a great number of cases and has been used by Lea[3] in explaining the solubility of urease after treating the torula of urine with alcohol; by Buchner[3] for the release of zymase from yeast cells by grinding with sand and kieselguhr; by Albert[4] for the same result by treatment with acetone; by Pottevin and Napias[3] to explain the discrepancies between Fernbach and O'Sullivan with regard to the liberation of invertase by various yeasts; and by many others, but always to explain the same phenomenon of an enzyme not being yielded to the solvent, until after some special treatment of the cells containing it. Later I shall discuss some of these cases in detail.

For the purpose of this investigation we may consider the plant cell to be made up of two layers. The outer cell wall is composed chiefly of hemicellulose, true cellulose, lignin, and cutin, the lignin, according to König,[5] increasing with the age of the cell and at the expense of true cellulose. This outer wall acts much like a filter, allowing practically any substance in solution to pass. Within this outer cellulose wall and closely adherent

[1] Proinvertase reversibilita dell invertasi nei Mucor, *Rend. Accad. Lincei. Roma*, 15, I Sem., 587 (1906); Abst. in *Bot. Centb.*, **105**, 245 (1907).

[2] *Ber.*, **1871**, 810. Report of the Rostock meeting by Victor Meyer.

[3] *Loc. cit.*

[4] *Ber.*, **35**, 2378 (1902).

[5] *Landw. Ver. Sta.*, **65**, 55, 65 (1907).

to it, probably secreting it, lies the outer protoplasmic layer, the plasmotic membrane or *Hautschicht.*[1] So long as the protoplasm is living, this plasmotic membrane acts like a semipermeable membrane, allowing the free passage of water but tenaciously holding most other substances. On the death of the protoplasm the plasmotic membrane loses its semipermeable properties and allows various substances to pass it freely; that is, the protoplasm no longer plasmolyzes. It would seem then, that any treatment which killed the protoplasm would liberate the enzyme, and that appears to take place in many cases, although not in all.[2]

At this point we must take into consideration the work of Iscovesco[3] on the passage of colloids through colloids as applied to cell specificity. Iscovesco has shown that one colloid may penetrate another when they bear electric charges of the same sign, but not when the signs are opposite. The sign may be changed by changing the chemical composition of the surrounding medium. It is thus plausible that treatment with various agents might change the sign of the charge borne either by the protoplasmic wall or by the enzyme, and thus render the cell permeable.

Pantanelli[3] also has recently studied the permeability of the cell wall by observing the effects of colloids on the formation and excretion of invertase, and by comparing the permeability of the wall to certain salts at the time when enzyme secretion was at its maximum. He holds that the secretion of the enzyme into the surrounding medium is a function of the living cell, being made possible by autoregulation of the permeability of the protoplasmic cell wall, and that this change is reversible. Thus he finds the invertase of yeast and of *Mucors* to be the only true ektoenzymes, since in others the escape of the enzyme from the cell is conditioned by the dying of the cell itself. Some colloids, as gum arabic and peptone, in the culture medium stop the intracellular formation and secretion of invertase. The secretion is at a maximum during the time of maximum fermentation, and at the same time the permeability of the cell wall to certain salts is also greatest. In the case of *Mucor stolonifer*, the appearance of the invertase in the surrounding medium is due rather to the enzyme being given off by the dead tissue, because it corresponds in time with spore formation and is wanting in the earlier stages of development, at which period cane sugar as such is taken up. The general facts here correspond closely with those for the date as well as for *Penicillium*, the invertase passing into the solution readily at the time of maturity. In the case of *Mucor* there seems to be no adequate ground for supposing that increased permeability of the cell wall to inorganic salts would indicate increased permeability to inver-

[1] Jost, Pflanzenphysiologie, Vorl. 2.
[2] Buchner and Meisenheimer, *Z. physiol. Chem.*, 40, 167.
[3] *Compt. rend. soc. biol.*, 62, 625.
[4] *Ann. di Bot.*, 3, 113 (1905); Abst. in *Bot. Centb.*, 105, 185

tase, although it might be true. There is, however, no ground to believe that the invertase, prior to its time of secretion, did not exist in an insoluble state. While I am not in a position to disprove impermeability in every case, it certainly does not conform to the facts for the green date.

It is significant that observations heretofore on the persistency with which cells often retain the enzyme have been made, with few exceptions, on unicellular plants. In these cases the cell walls are more resisting than those of soft complex tissues, and a process similar to Buchner's would be required to break open any considerable number of them. The conditions in the interior of a green date, however, are quite different. Here the heavy cellular walls found in the yeasts and other unicellular plants are not needed for protection; therefore grinding and crushing by ordinary means should allow the escape of at least detectable amounts of invertase. Especially is this true, since the cells of a complex tissue are more or less torn and cannot glide about freely among one another like yeast cells. The juice pressed from such bruised tissues contains a very large percentage of all the water present in the fruit, and with it, sugar, protein, and other soluble cell constituents, which are otherwise held by the semipermeable plasmotic membrane. Under these conditions it is hardly possible to believe that invertase exists in solution in the cell sap. The retention of a great amount of invertase by the ripe date pulp which cannot be removed by prolonged washing with water, a similar partial retention of invertase by the rootlets of seedlings and of catalase by cured tobacco, also speak against retention by impermeability.

Another fact which points to the insolubility of the invertase is the behavior of green date tissue toward such substances, as ether, chloroform, toluene,[1] etc., with regard to the subsequent solubility of the enzyme. It was mentioned above that, on the death of protoplasm, the plasmotic membrane ceases to be semipermeable and allows the passage of most substances as freely as does the cellulose wall. If the enzymes in general are in solution in the cell sap, then by treatment with protoplasmic poisons they should be released. The instances already cited of various enzymes being released by treatment with alcohol, acetone, toluene, etc., might well be due to this effect. Fischer and Lindner,[2] however, failed to liberate invertase from *Monilia candida* by this process. The green date also fails to give up its invertase after killing with these substances.

Samples of ground green date, from which the inactive juice had been largely removed by pressure, were treated over night in closed vessels with acetone, ether, toluene, and chloroform, respectively. After exposing in the air until all traces of the added material had disappeared, they were macerated with water for two days and the aqueous extracts tested for

[1] E. Fischer, *Z. physiol. Chem.*, **26**, 75 (1898).

[2] *Ber.*, **28**, 3034.

inverting power with negative results in all cases. The residues were extracted seven days longer with very frequent changes of water, and their inverting power determined. It did not seem to be in any degree impaired. A microscopic examination showed the protoplasm drawn away from the cellulose wall and collected in small dense masses within the dead cell. A second test on the inner tannin-free portion of Rhars date from which the sugar had been extracted with water was made by digesting two weeks in a large volume of ether. After decanting the ether, the pulp was dried in the air and then soaked in water several days. The extract obtained in this way was found to be inactive, but the residue showed very active properties. An attempt was also made to liberate the invertase by heat.[1] A portion of the inner tannin-free material was extracted to remove sugar and insoluble materials, dried *in vacuo* over sulphuric acid and finally heated to 145-150° C. in a hot air oven for 45 minutes. The activity of the pulp was much impaired, but no active extracts could be prepared from it. In all these cases the protoplasm must have been killed and more or less broken down, so that the retention of the invertase could not have been due to impermeability of the cell wall. Considering all these facts we find any other explanation, than that the invertase is insoluble, very difficult to maintain.

The acceptance of insoluble invertase is not so easy because the concept, enzyme, carries with it the idea of solubility. This undoubtedly follows from the use of the term enzyme synonymously with soluble ferment or unorganized ferment, in contradistinction to organized ferment which involves the idea of living matter and is necessarily insoluble.

Before further consideration of the subject it will be well to recall the condition under which an enzymic action may take place. Barring temperature, alkaline or acid reaction, etc., the essential condition is to establish molecular contact. There are four cases:

First, soluble enzyme and soluble substance to be acted upon; reaction follows. Invertase and cane sugar.

Second, soluble enzyme and insoluble substance to be acted upon. Diastase and starch.

Third, insoluble enzyme and soluble substance to be acted upon. Green date invertase or artificially precipitated invertase and cane sugar.

Fourth, insoluble enzyme and insoluble substance to be acted upon; no reaction. Diastase of ungerminated grain and starch granules, and probably many enzymes which have been recognized as existing in the zymogen state.

Insoluble Compounds of Invertase.

That invertase in the green date exists in an insoluble condition but retains all the catalytic properties of the soluble enzyme seems entirely possi-

[1] Buchner, *Ber.*, 30, 117, 120.

ble. Loew[1] has shown catalase also to exist in two modifications. The insoluble catalase he believes to be a nucleoprotein compound of the soluble form. The writer has already called attention to the fact that tannin does not retard the action of date invertase, although in aqueous solutions the tannin-invertase compound may be filtered off. The tannin-enzyme precipitate, whatever its nature, retains its original catalytic properties. A similar result was observed in the case of the lead subacetate precipitate of date extract. A number of samples of date extract—cane sugar solution mixture was prepared as follows: 40 cc. of glycerol extract of Birket ei Haggi date were mixed with 1000 cc. of sugar solution, samples of 85 cc. each were removed with a pipette, placed in 100 cc. flasks, 1 cc. of lead subacetate added to each flask and the mixed contents diluted to 100 cc. Half the samples were filtered at once and the remaining half allowed to stand in contact with the precipitate. One sample from each of the sets was polarized from time to time. Those which stood in contact with the lead precipitate were inverted rapidly, while those from which the precipitate had been removed by filtration were unaffected. The retardation is scarcely more than would be expected from the poisonous effect of the lead on the enzyme as noted by Bokorny for metallic salts in general.

RATE OF INVERSION OF CANE SUGAR BY THE LEAD SUBACETATE DATE EXTRACT PRECIPITATE.

Hours.	Filtered.	Unfiltered.
Initial reading	+13.96	+13.96
18	+14.02	+11.64
42	+14.02	+ 9.62
90	+14.08	+ 4.80
234	+13.70[2]	— 2.22
330	+13.35	— 4.96

The chemical nature of the tannin and lead subacetate precipitates is not known. They may be true chemical compounds with the enzyme itself, such as are formed with the other protein matter, or the removal of the enzyme may have been mechanical, due to adsorption. In either case the enzyme was removed from the solution, but ceased its catalytic activities only after the removal of the precipitate. It is not improbable that compounds of the enzyme could be formed which, while insoluble, would retain all the catalytic properties of the original, provided the substrat was soluble. In other words, the chemical nature of the enzyme molecule as a whole could be changed easily so as to affect its solubility without affecting that portion in which the catalytic properties reside.

[1] Catalase, *U. S. Dept. Agr. Report*, 68, 1901.

[2] The filtered mixture did not remain sterile but became quite turbid after about one week, hence the slight inversion after that time. Had the slight inversion noticed been due to invertase not precipitated by the lead subacetate, its effect would have been most marked in the first hours of action instead of first becoming noticeable after ten days. Microscopic examination showed great numbers of *cocci*.

Hedin[1] has observed that casein solution in 0.2 per cent. sodium carbonate is digested by contact with trypsin adsorbed in charcoal. He finds that the casein actually takes up trypsin from the charcoal and that the trypsin can then be removed by filtration, retaining its proteolytic properties. This he believes to be due to a non-adsorbable compound of the enzyme with the substrat. Such a compound does not seem to exist between cane sugar and date invertase, because the lead subacetate removes all the invertase, even in the presence of cane sugar. If such an invertase-cane sugar compound does exist, it is carried down completely with the lead subacetate precipitate.

Hedin[2] has also studied the selective adsorption of the enzymes and has separated α- and β-protease of ox spleen by adsorption in charcoal. Application is then made of this principle to explain why sometimes more enzyme is obtained by Buchner's process than by others. He suggests that probably kieselguhr and perhaps also the cell residues act adsorptively. One might infer from this, that in the case of the green date, the invertase was held back by simple adsorption. The retention of the enzyme by the green cells, however, is too complete to admit of explanation in this way. Furthermore, if adsorption by the cell residues were responsible, we should not expect so profound a change in the adsorption powers at the time of ripening. I am inclined to believe that the retention of the enzyme as an endoenzyme up to the moment of ripening, has a deeper physiological significance than to be merely accidental to our methods of extraction. I do not contend that no adsorption takes place, for it probably does; but I do not believe that adsorption in the sense used by Hedin could take place almost momentarily and completely.

Insolubility of the invertase during the green stages thus seems to be the only theory which explains the actual facts observed. To determine the mechanism of this insoluble state, however, will require much further investigation. We suggest, tentatively, two general ways in which it could be accomplished by the plant. The enzyme may exist in combination with some other substance and move about freely in the cell sap without being in solution. This hypothetical compound might take the form of dense, minute, or even ultramicroscopic particles, or it might be indefinitely expanded until it occupies the same limits as the medium in which it is suspended, similar to the way caseinogen in milk is supposed to be expanded by the help of calcium phosphate. Along this line, but seemingly less probable, is the recent theory held by Hofmeister and Jacoby.[3] They believe the endoenzyme is localized in vacuoles which are kept isolated by a thin layer of colloid. I fully agree with this idea in so far as it concerns localization,

[1] *Biochem. Jour.*, 1, 484 (1906).
[2] *Ibid.*, 2, 81.
[3] Oppenheimer, Die Fermente, p. 73.

but rather in the manner to be described later under the second possibility. Such a compound would be under the direct control of the cell and could be broken down, leaving the free enzyme in true colloidal solution and capable of passing the protoplasmic layer, which, heretofore, had acted as a filter. In this way there could exist simultaneously both soluble and insoluble enzyme exhibiting the same properties.

The second possibility is that the enzyme is held in some insoluble combination by the protoplasm. This theory was first proposed by E. Fischer for the invertase of Monilia, and seems to the writer to be the most tenable of all, after certain modification. As is well known the protoplasm is exceedingly complex, histologically, being made up of innumerable fine threads and granules. Certain of the granules may be the seat of one enzyme and others of another. This accomplishes the same purpose as the vacuoles suggested by Hofmeister and Jacoby. The enzyme-protoplasm compound which I have assumed to exist, whether it be simple adsorption or a loose chemical combination does not necessitate living protoplasm. The writer therefore suggests the following theory for those cases where endoenzymes exist.

The enzyme is in combination with some constituent of the protoplasm. This combination modifies the enzyme molecule so as to render it insoluble, without, however, affecting its catalytic properties, provided the substrat is soluble. The enzyme-protoplasm compound may or may not break down on the death of the protoplasm. The protoplasm may and usually does liberate the enzyme about the time of maturity of the cell. Slow decomposition, autolysis, or external chemical or physical influence may render the enzyme soluble. The latter possibly act by destroying the integrity of the cell, thus allowing more intimate mixing of the contents and the consequent liberation of the enzyme before its proper time.

Zymase.

The theory outlined above seems to explain adequately the phenomena observed with zymase. Buchner[1] advances and successfully answers three objections which might possibly be raised against his theory of fermentation without living yeast cells. Firstly, the fermentation may have been due to bacteria or yeast cells. Secondly, the evolution of carbon dioxide may have been due to some process other than alcoholic fermentation. Thirdly, the fermentation may have been due to small pieces of living protoplasm passing through the filters.

The idea that zymase exists within the cell as an insoluble compound is not at variance with the observed facts, nor does it invalidate the theory of cell-free or life-free fermentation. If Hans Buchner[2] had maintained that

[1] Lecture before Deutschen Chem. Gesell., *Ber.*, 31, 568.

[2] *Münchener medic. Wochenschr.*, 1897, 322.

the fermentation was due to a ferment held in combination by the protoplasm instead of attributing it to particles of the living protoplasm, his objections would not have been answered so easily. Microscopic examinations have shown the entire protoplasmic content of many of the cells to be forced out into the juice by Buchner's process. Thus his results with yeast cells may be explained in two ways other than assuming soluble zymase to exist within the unbroken cell. Some of the insoluble compound may have been easily comminuted till it passed the finest filters. The fact that Buchner sometimes observed 90 per cent. of the activity of his juice to be removed by filtration, speaks for this theory. He attributed the fact to adsorption. Other observers[1] have found the juice to be rendered inactive by similar treatment. Another explanation of Buchner's results may be that by destroying the integrity of the cell, some other substance, probably a protease which has been held isolated by the living protoplasm, comes into contact with the enzyme-protoplasm compound and splits it up. The fact that zymase is rapidly destroyed by a protease after it is extracted from the cell and that it is shielded by adding another protein, such as serum albumin, favors this view.[2] Furthermore the green date which yields no soluble invertase when killed by acetone, chloroform, etc., was found by Slade, while working upon the identification of the enzymes of the date, to contain no, at least only occasionally, traces of protease.

Vegetable Ereptase.

The work of Vines[3] on the vegetable protease requires a somewhat different interpretation when we consider the probability of an insoluble protease. All the phenomena that Vines attributes to vegetable ereptase in his earlier papers can be explained quite as readily by assuming an insoluble protease. As he states, at that time he had never gotten the peptic reaction unaccompanied by the tryptic, but frequently the latter without the former.[4] The peptic reaction is determined by the disappearance of a clot of fibrin, an effect which could never be brought about by an insoluble enzyme. The ereptase reaction is determined by the production of tryptophane from peptone, which could take place easily with an insoluble enzyme. His main indication of the existence of ereptase depends upon the difference in the time of appearance of the two reactions.[5] A clot of fibrin is suspended over ground bean; no reaction takes place till about the 9th day, after which the clot quickly disappears. The same bean material gave the tryptophane reaction with peptone at once. This is exactly what would occur if the bean contained an

[1] Stavenhagen, *Ber.*, 30, 2422.
[2] Hardin, *Ber.*, 36, 715.
[3] *Loc. cit.*
[4] Vines, *Ann. of Bot.*, 1905, 169, 175.
[5] *Ibid.*, 20, 113, 118 (1906).

insoluble protease which became soluble later. Another indication he finds in the different effect of sodium carbonate on the two reactions when yeast was used.[1] The tryptophane reaction took place readily with a small amount of yeast and relatively large amount of sodium carbonate. On the other hand, a fibrin clot was first appreciably attacked in the presence of 2 per cent. sodium carbonate when 20 per cent. of yeast was present. This is to be expected if an insoluble protease were present which was slowly passing into the solution or even if a soluble protease existed within and was escaping slowly from the yeast cells. Even though the speed of reaction by which sodium carbonate destroyed the protease were very great, some tryptophane would be produced from the peptone, since the chances for molecular contact are very great, because both substances are soluble. On the other hand, contact between protease and fibrin clot would take place only with the molecules on the surface of the latter, a relatively small number, and furthermore the enzyme must travel through a layer of sodium carbonate solution before reaching the fibrin. Thus only when protease molecules in overwhelming number are present can there be any appreciable effect on the fibrin clot.

Recently Vines[2] has succeeded, however, in isolating a purely peptic enzyme from hemp seed. This admittedly renders probable the existence of vegetable ereptase, but does not answer the foregoing objections to his former experiments.

Summary.

The invertase of the date remains insoluble in all ordinary solvents throughout its green stages but becomes readily soluble on ripening. The change in the behavior of the invertase toward solvents coincides very closely in point of time with the passage of the tannin into the insoluble form. Tannin in relatively large amounts does not retard the action of date invertase either in the extract or in the pulp. Soluble tannin, however, hinders the solution of date invertase in water but the invertase can be extracted by glycerol, provided the glycerol is added at the same time the tannin is added. Green date invertase cannot be extracted by crushing and macerating the green fruit with glycerol, therefore the invertase is not rendered insoluble by the escape of soluble tannin on crushing the tannin cells. This conclusion is confirmed by the behavior of the invertase in the tannin-free portion of the date after the tannin-bearing tissues have been completely removed. There is no direct connection between the change in the state of the tannin and that of the invertase.

The inversion of cane sugar by the green date pulp is not accomplished by the living protoplasm liberating a soluble ferment from a pre-existing insoluble zymogen or by rendering active a proferment. The rate of inver-

[1] *Ann. of Bot.*, **289**, 305 (1904).

[2] *Ibid.*, **22**, 103.

sion by equivalent amounts of green and ripe pulp of the same variety are practically identical. Protoplasmic poisons—picric acid, chromic acid, and formaldehyde—retard the action of green and ripe pulp but to approximately the same degree. If the living protoplasm were in any way connected with the inversion, the retardation would be greatly intensified in the case of green date. Green date tissue is not rendered inactive by soaking in ether, chloroform, acetone, etc.

The inner tissues of the green date are composed of relatively tender walled cells, which, unlike those of yeast and unicellular plants, are fixed and cannot glide about freely among themselves; consequently by ordinary grinding, appreciable numbers are broken up and yield their soluble contents to water or glycerol. The press juices contain most of the water in the fruit and large amounts of soluble substances which are usually retained by the healthy and unbroken semipermeable plasmotic membrane. These juices and extracts are invariably free from invertase until the fruit ripens, although the press residues are always very active.

Treatment of the tannin-free green date tissue with chloroform, ether, toluene and acetone causes the protoplasm to collect in granules but does not alter the behavior of the invertase towards solvents. Moreover, the invertase is not liberated by heat. This treatment should destroy the semipermeable nature of the plasmotic membrane. From these observations, the theory of the impermeability of the cell wall for the invertase of green date is untenable.

Enzymic action will take place whenever either enzyme or material to be acted upon is soluble; that is, molecular contact must be established. Tannin removes the invertase of green dates from solution, but inversion is not checked unless the precipitate is filtered off. Date extracts precipitated by lead subacetate still invert cane sugar, but on removing the precipitate inversion is stopped. It is then possible to invert sugar by means of invertase artificially rendered insoluble.

In the place of impermeability of the cell wall to the enzyme, the writer proposes the following theory. It is highly probable that green date invertase and possibly other endoenzymes are held in an insoluble combination by some constituent of the protoplasm. In some cases this combination may be broken down and the enzyme pass into solution while the protoplasm is living, but in others the combination may persist, even after the death of the protoplasm. The enzyme may be rendered soluble also by external chemical or physical influence. These probably act by destroying the integrity of the cell and allowing the contact of substances which have been localized by the living protoplasm. On maturity of the tissues the enzyme is generally liberated, possibly by autodigestion or other profound change in the protoplasm.

In order to establish the impermeability of the cell wall to the enzyme in

any given case it must be shown that the enzyme is in solution in the cell sap and not held in combination by the protoplasm.

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NOTE ON THE DYER METHOD FOR THE DETERMINATION OF PLANT FOOD IN SOILS.[1]

BY FRANK T. SHUTT AND A. T. CHARRON.

Received March 24, 1908.

During the past twenty years or so the problem of soil fertility has received much attention from chemists, physicists and biologists, and as a result there is to-day a clearer understanding as to what constitutes productiveness in a soil—its several factors and their relative importance—than there was a quarter of a century ago. We did not then recognize that the chemical data formed but one factor in soil diagnosis; that texture, moisture-holding capacity, bacterial life, drainage, precipitation, etc., must all be considered before drawing any conclusion as to a soil's probable productiveness. It was this neglect that caused doubt on all sides to be entertained as to the practical value of soil analysis, and indeed the agricultural chemist himself had well-nigh abandoned all hope of being able to interpret his own data for the benefit of the farmer. Though we are yet far from having soil diagnosis on a thoroughly satisfactory basis, a distinct advance has been made and the writers feel that one of the most prominent and valuable features of this diagnosis lies in the determination and recognition of the soil's store of more or less available plant food.

In so far as the soil's crop-producing power or the need of special fertilization can be determined by chemical means, the estimation of the plant food present in a condition more or less available for crop use must be a matter of considerable importance. The stores of insoluble, inert plant food, no matter how large, can be of but little value to the growing crop; it is rather those small percentages of potash, phosphoric acid, etc., that are at once capable of being utilized by plants that serve to measure the soil's immediate ability to sustain vegetable life. In these two classes we have represented what might be termed latent and potential fertility, though, of course, no strong line of demarkation can be drawn between them—the former being always converted into the latter, gradually but with varying rapidity, according to a number of conditions which we need not now discuss.

In 1894 Dr. Bernard Dyer, working on soils from the Rothamsted Experiment Station, the history of which as regards manuring and crop yields was well known, proposed the use of a 1 per cent. solution of citric acid as a solvent for the available phosphoric acid and potash.

[1] Read at the Chicago meeting of the American Chemical Society.

His analytical data were well in accord with the field results and from the percentages obtained he was able to establish minimum and maximum limits regarding the necessity and non-necessity of phosphatic and potassic fertilizers. Further, he found that the sap of the rootlets of a number of farm plants had an average acidity approximately equivalent to that of 1 per cent. citric acid solution, thereby in a large measure confirming the correctness of his deductions respecting the value of the solvent proposed.[1]

Since that date, various solvents have been proposed, more especially in the United States. Several of these were experimented with in the laboratories of the Dominion Experimental Farms, Ottawa, but as they appeared to lack that evidence which had been brought forward to support the Dyer method, it has been the latter process that has always been employed in our official soil investigations. Dyer's limits have not been found to answer invariably, but this is only what might have been expected; the general nature of the soil must be taken into account, its geological origin and the climatic conditions of the district considered. On the whole, however, the method and proposed limits have proved very satisfactory. Possibly it is only a tentative method, but the fact remains that as data accumulate from workers in different parts of the world, its claims to represent the amounts of more or less readily assimilable mineral plant food in the soil receive corroboration.

Within the past two months the writers, in working on certain virgin prairie soils from the Northwestern provinces of the Dominion, have thought it desirable to ascertain how far the results might be affected by certain modifications of the original method as described by Dyer. These modifications were in the reduction of the time during which the solvent was in contact with the soil and in the reduction of the volume of solvent used per unit of air-dried soil, to obviate the necessity of evaporating large volumes of solution. Dyer's method calls for an extraction period of seven days, during the first six of which the mixture is kept constantly agitated, 1000 cc. of solvent being used per 100 grams of soil.

The soil sample was of a composite character, made up of 8 samples collected (at Tisdale, Sask.) on as many dates between June 15th and October 20, 1907. It represented the native prairie soil to a depth of 8 inches. The soil had been "broken" in 1906, and this season (1907) bore a crop of wheat. It might be described as a rich, black loam in which sand predominated and typical of large areas in the Canadian Northwestern wheat belt. Analysis showed it to contain large percentages of semi-decayed vegetable matter and nitrogen, a characteristic feature of these prairie soils.

The analysis of the air-dried soil, according to the method of the A.

[1] *J. Chem. Soc.*, **65**, 115–167 (1894).

O. A. C., using 1.115 sp. gr. hydrochloric acid as the solvent, afforded the following data:

	Per cent.
Moisture	6.26
Organic and volatile matter	13.34
Insoluble matter, clay, sand, etc.	68.49
Oxide of iron and alumina	8.68
Lime (CaO)	1.04
Magnesia (MgO)	0.86
Potash (K_2O)	0 58
Phosphoric acid (P_2O_5)	0.19
Carbonic acid, etc. (undetermined)	0.56
	100.00
Nitrogen, in organic matter	0.45

From these results we may conclude that as regards the stores of latent plant food, the soil is one very well supplied with nitrogen and potash; that phosphoric acid is present in fair amounts and that lime exists in quantities sufficient for crop needs.

In the subjoined tabular statement the results obtained by the modifications of the Dyer process already referred to, are presented, the percentages of lime being given in addition to those of phosphoric acid and potash. All the data are averages from at least two closely concordant determinations:

INFLUENCE OF TIME OF DIGESTION.

(Solvent: 1% Citric Acid Solution.)

	Phosphoric acid (P_2O_5). Per cent.	Potash (K_2O). Per cent.	Lime (CaO). Per cent.
100 grams soil in 1000 cc. 7 days	0.02287	0.03818	0.5320
100 grams soil in 1000 cc. 5 hours	0.01807	0.03958	0.5210
100 grams soil in 500 cc. 7 days	0.01999	0.03355	0.2718
100 grams soil in 500 cc. 5 hours	0.01599	0.03089	0.2285

Comparing first the data from the analyses made when using 1000 cc. of the solvent, it will be noticed that reducing the period of digestion from 7 days to 5 hours materially decreased the amount of phosphoric acid dissolved, but did not similarly affect the potash—the percentages of the latter being practically identical for both periods. The lime falls off but slightly with the shorter digestion.

Employing 500 cc. as the volume of solvent, the phosphoric acid percentages present practically the same differences as those already noted—in other words, slightly higher amounts were obtained from the longer digestion. Five hours' digestion gave a somewhat lower percentage of potash than 7 days, but the difference is almost within the limit of experimental error. The lime dissolved is markedly less for the shorter period.

INFLUENCE OF VOLUME OF SOLVENT.

(Solvent: 1% Citric Acid Solution.)

	Phosphoric acid (P_2O_5). Per cent.	Potash (K_2O). Per cent.	Lime (CaO). Per cent.
100 grams soil in 1000 cc. 7 days.....	0.02287	0.03818	0.5320
100 grams soil in 500 cc. 7 days.....	0.01999	0.03355	0.2718
100 grams soil in 1000 cc. 5 hours.....	0.01807	0.03958	0.5210
100 grams soil in 500 cc. 5 hours.....	0.01599	0.03089	0.2285

In this table are given the same data as in the preceding, but they are arranged to more readily show the influence of the volume of solvent. No detailed discussion of these data is necessary; a glance at the figures is sufficient to make apparent the only conclusion that can be reached, *viz.*, that reducing the volume of solvent used, materially decreases the percentages of phosphoric acid and potash obtained. In the case of lime, the smaller volume extracted but one-half that taken out by the larger volume. Clearly the influence of volume of solvent is decidedly greater than that of the period of extraction.

No doubt soils of a different character would not yield results that would fall exactly into line with those here recorded, that is, as to the effect of varying the period of extraction and the volume of the solvent on the amount of mineral matter dissolved, but the general trend would, we believe, be the same. It seems highly desirable that further data on this important question of available plant food should be obtained from widely different points and correlated with the field results. These analytical data should be, as far as is practicable, strictly comparable, and to this end it is evidently necessary that the details of the process as regards period of extraction and volume of solvent, should be carried out alike by all workers. There seems to be every reason for adherence, in these respects, to the time and volume as given by Dr. Dyer in his original account of the process.

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SOME OBSERVATIONS ON THE ASSAY OF TELLURIDE ORES.

BY GEORGE BORROWMAN.

Received April 4, 1908.

Much has been written concerning the assaying of telluride gold and silver ores, yet the literature affords striking contradictions as well as statements unsupported by experimental data. However, there seems to be agreement in the opinion that tellurium is the cause of serious irregularities. Mr. A. L. Davis, in *Tech. Quart.*, *Vol. XII*, sums up the situation as follows: "As to the percentage of loss sustained in work, whether by scorification or crucible method, many experiments carried out upon the foregoing lines indicate to me that nothing definite can be

laid down in regard to it. Every ore, every slag, every scorification, every cupel, let alone the temperature at which the assay is carried on, has some effect upon the loss and these make too many unknown quantities to arrive at any conclusion."

It was the purpose of the writer in the work here recorded to ascertain a few facts concerning the effect of tellurium in the crucible assay for gold. The points investigated were: loss in the slag; loss in cupellation; the effect of variation in temperature of fusion.

The ore selected for the experiments was a high-grade telluride gathered from various parts of Colorado, rich in silver, gold and tellurium. With the sulphuric acid test it gave a very strong indication of the latter element and analysis showed the presence of 10.5 per cent. chiefly as hessite and sylvanite. The gangue was silicious, consisting of quartz, feldspar and a little calcite. The ore had a reducing power of about 1.5.

The material was ground very fine, first through 120 mesh sieve, then in agate till all passed through bolting-cloth. In all the work 1/10 A. T. was taken for each assay, the samples being weighed out on a quantitative balance instead of on the usual pulp scales. All fusions were made in a muffle at about 1200° excepting in Series No. 4; all the fluxes were passed through a 40-mesh sieve mixed with the ore till thoroughly homogeneous. In short, the greatest care was taken to eliminate all variations except the one studied.

Experiments were first conducted to learn the influence of tellurium in carrying gold into the slag. Mr. C. H. Fulton, in THIS JOURNAL, **20**, 586, records data to show that slag losses in telluride fusions are much greater than in ordinary gold ore crucible work. Messrs. Hillebrand and Allen, *Bulletin No.* **253**, *U. S. Geological Survey*, find losses insignificant, and commenting on the work of Mr. Fulton suggest that his losses might have been due to the use of iron nails in the fusions.

In the investigation of this point a series of assays was first made on the raw ore, using the following charge:

Ore 1/10 A. T.	
Litharge	90 g.
Silica	10 g.
Argols	2½g.
Sodium bicarbonate	30 g.
Salt cover.	

Another series was then made on ore from which the tellurium had been removed. In removing it use was made of the fact that nitric acid dissolves tellurium and silver in a telluride and leaves the gold in the residue. Each sample was boiled with nitric acid (1.27) till no further action was apparent; the residue was washed and dried and fluxed under the same conditions as maintained in the first series. Enough silver

was added to the de-tellurized series to replace what had been removed by the acid. The slags from each series were then carefully ground and assayed, using the following charge:

Slag	
Litharge	30 g.
Argols	2 g.
Salt cover	

The buttons from both the ores and slags were cupelled. The results are set down in the following tables:

SERIES No. 1.

No.	Ore. Mg. gold found.	Ore. Oz. gold per ton.	Slag. Gold found.
1	16.14	161.4	None
2	16.18	161.8	"
3	16.18	161.8	"
4	16.23	162.3	"
Av.....	16.18	161.8	

SERIES No. 2.

No.	Ore. Mg. gold found.	Ore. Oz. gold per ton.	Slag. Gold found.
1	16.10	161.00	Trace
2	16.16	161.60	None
3	16.20	162.0	Trace
4	16.11	161.10	None
Av.....	16.14	161.4	

From the above data it is obvious that the influence of tellurium in carrying gold into the slag is very slight, if there is any; the amount recovered was in no case weighable.

The effect of tellurium in cupellation was next investigated, and incidentally the functions of litharge in the fusion. On the assumption that the tellurium in a crucible charge is oxidized by the litharge and carried into the slag, a series of charges was made up varying this constitutent from 90 to 180 grams. Theoretically the amount of tellurium carried into the button as a lead alloy should be in inverse ratio to the amount of litharge in the fusion. A series of four samples was made in duplicate. The buttons of one series were dissolved in nitric acid and the tellurium determined by precipitating it in hydrochloric acid solution with sulphur dioxide. The other series was cupelled for gold. The two duplicates are considered as one series, *i. e.*, No. 3.

SERIES No. 3.

No.	Grams. PbO in charge.	Mg. Te in button.	Mg. gold found.	Oz. gold per ton.
1	90	lost	16.10	161.00
2	120	287.5	16.24	162.24
3	150	298.9	16.18	161.80
4	180	176.8	16.15	161.50
Average.....			16.17	161.70

All of the beads of the above series were frosted, showing the presence of tellurium, notwithstanding the great excess of litharge in the fusion. It would then seem that litharge in reasonable amount is inadequate to slag off all the tellurium in this ore. The loss of gold, however, was inconsiderable, the average of the series varying but 0.01 mg. from the average of Series No. 1 in which the tellurium had been removed previous to fusion. These results are at variance with published statements regarding tellurium in cupellation. Messrs. T. J. Eager and W. W. Welch, however, found that no loss occurred in the presence of the element up to, 10 per cent. The amounts in the above experiment are many times that. A bead from an assay, duplicate of No. 1 in the above series which was also the same as those of Series No. 2, was tested quantitatively for tellurium and 6.9 mg. were found; so that it may be present even in the bead in considerable amount without there being more than a negligible loss of gold.

The work was concluded with some experiments to learn the effect of variation of temperature of fusion on gold recovered and the amount of tellurium carried into the button. Some assayers recommend an extremely high temperature. Mr. R. W. Lodge, however, in his "Notes on Assaying," states that he believes high temperatures break up some tellurium compounds in the slag with a consequent alloying of the element with the lead.

A series of four was run in duplicate consisting of charges made up exactly as those of Series No. 2. The temperature was varied between 800° and 1600°. As in the previous experiment the buttons from one set were cupelled for gold, the other dissolved in nitric acid and assayed for tellurium.

SERIES NO. 4.

No.	Temperature.	Wt. of buttons.	Gold found. Mg.	Gold per ton. Oz.	Tellurium found. Mg.
1	800° C.	30.5	16.10	161.00	258.2
2	1000° C.	32.5	16.16	161.60	150.0
3	1250° C.	32.8	16.20	162.00	195.6
4	1600° C.	32.8	16.16	161.60	215.9
	Average.....		16.16	161.60	

The irregularities in the amounts of tellurium could not be accounted for, yet it seems improbable that the amount varies directly with the temperature. As to the gold the yield is greatest at about 1200°, though the average of the series is but slightly below that of Series No. 1.

Summary.

The foregoing data seem to warrant the conclusion that tellurium as the cause of irregularities in crucible work has been overestimated. Slag losses are no greater than in ordinary gold ores; the element may be present in the lead button in relatively large amounts with no consider-

able percentage of loss. The presence of tellurium in the bead does not necessarily imply a loss of gold in the cupellation though, of course, a frosted bead would not be permissible when silver is to be determined. In high-grade tellurides when silver is to be estimated, the writer suggests a preliminary treatment with nitric acid, with subsequent precipitation of the silver as chloride which may be dried and added with the residue from the acid treatment to the fluxes in the crucible. Variation in temperature of fusion does not seem to be of great moment though the data above are most favorable to a temperature of about 1200°.

The average obtained from Series No. 1 is higher than that obtained in the others showing a loss due to tellurium in fusion and cupellation, yet the variation is small, the average of No. 1 being not more than 0.24 per cent. higher than the lowest average, that of Series No. 2. The members of the various series differ among themselves in some cases considerably, but perhaps not more than would be expected in any high-grade ore, owing to lack of homogeneity of sample. In the opinion of the writer, irregularities in high-grade tellurides are due more to this lack of homogeneity than to tellurium. It is conceivable that in some ores the ratio of gold to tellurium might be much less and hence the percentage of loss greater. In such cases a preliminary treatment with nitric acid to remove the tellurium would obviate the difficulty.

UNIVERSITY OF NEBRASKA,
LINCOLN, NEB.

THE DETERIORATION OF COAL.

BY S. W. PARR AND W. F. WHEELER.

Received April 7, 1908.

In coöperation with the State Geological Survey and the Engineering Experiment Station of The University of Illinois, certain facts have developed which bear directly upon the behavior of coal. They are of considerable moment and should be taken into account in any study of this material. The first pertains to a deterioration which cannot be ascribed to weathering processes, but rather to the simple fact of the release of the material from the conditions which have surrounded it in the seam. This has been recognized in a rather indefinite way from time to time, but without data to substantiate the fact.[1]

The following items are given in support of this theory of loss. In the summer of 1900 twenty-nine samples of coal were collected at the face of the vein, quartered in the usual manner, placed in galvanized iron cans with screw cap and tire-tape seal, exactly as described by the Coal Testing Plant of the United States Geological Survey.[2] They were

[1] THIS JOURNAL, 28, 650 (1906).

[2] *Bulletin No.* 261, *of the Coal Testing Plant, U. S. G. S.*

shipped directly to the laboratory, where they were transferred at once to one-quart jars of the "Lightning" or Putnam type, the coal being sufficient to practically fill the jars. This transfer was made with as much as possible of the original moisture retained in the coal. The "Lightning" jars were chosen because from extended experience with sodium peroxide, this jar was found to be the only container having a perfect seal. Twenty-one other samples were collected and sealed in the ordinary Mason jars.

After standing in the laboratory for about ten months, twenty-six of the "Lightning" jars, upon opening, showed a slight pressure of gas which ignited with a strong blue flame, burning from one-half to six inches in height above the top of the jar. Upon covering and retesting, these jars would reignite for two or three successive times. None of the samples sealed in the Mason jars would so ignite.

Two points are to be noted here, namely, that the coal content very nearly filled the jar and that the enclosure in the Putnam jar is practically that of a continuous glass seal, while the Mason jar is quite different as to the security with which the gasket is held and, in addition, has a large metallic surface exposed to the transmission of gases.

Another test pertains to the enclosing of the air-dried samples of the same coal in Putnam jars for more than eighteen months with the dry coal occupying about one-quarter of the jar. Upon opening, all of these jars showed a very positive evidence of the absorption of oxygen as indicated by the extinguishing of a lighted match. Analysis showed the presence of less than 1.5 per cent. oxygen and less than 2 per cent. of carbon dioxide.

TABLE NO. 1.—LOSS IN CALORIFIC VALUE DURING TRANSIT.

Test. No.	Locality.	Size of coal.	When sampled.	B.T.U. of ash, water and sulphur-free coal.	B.T U. Lost.
1	Westville	1¼ inch screenings	same day as mined	14684	
	"	" "	7 days after mining	14627	57
2	Springfield	" "	same day as mined	14478	
	"	" "	4 days after mining	14351	127
3	Herrin	1¾ inch screenings	same day as mined	14658	
	"	" "	6 days after mining	14553	105
4	Westville	3 inch nut	same day as mined	14768	
	"	3 " "	7 days after mining	14586	182
5	Springfield	3 " "	same day as mined	14655	
	"	3 " "	4 days after mining	14461	194
6	Herrin	3 " "	same day as mined	14751	
	"	3 " "	6 days after mining	14682	69

Another series of results related to the calorimetric determination of freshly mined coal and similar determinations made upon the coal after shipment in the cars in the ordinary manner. Six cars of coal were sampled at the mine while in the process of loading and calorimetric

determinations made on the samples so collected. After arrival at the University, the cars were sampled from the wagons as the cars were unloaded.

In the table above, the results are tabulated and attention is called to the fact that in each case there is a uniform drop in fuel values as between the freshly mined coal and that which had been subjected to transportation conditions.

Another series of results is given in Table No. 2, which is a comparison of values obtained at the St. Louis Coal Testing Plant of the United States Geological Survey, and samples from the same or near-by Illinois mines as determined in this laboratory. All conditions of operation were duplicated as nearly as possible, including the type of calorimeter, which was of the Mahler-Atwater design. Still, the results here, when reduced to the "ash, water and sulphur-free basis," were uniformly lower than those obtained at St. Louis. The only explanation seemed to lie in the fact that the samples here were held in laboratory storage longer than was the case with the St. Louis samples, our heat values being determined on the average after about 10 months of such storage. The extremes of difference lie between 1.6 per cent. and 3 per cent., but it is quite sufficient in amount to be a disturbing factor in basing conclusions on the behavior of coals of this type.

TABLE NO. 2.—COMPARISON OF U. S. G. S. WITH ILL. GEOL. SURV. VALUES.

U. S. G. S. No.	Ill. G. S. Lab. No.	Locality.	B.T.U. per lb. ash, water and sulphur-free coal.	Difference in B.T.U.	Per cent. of difference in B.T.U.
Ill. 1		O'Fallon	14567		
	95,96,97	" (a)	14214[1]	353	—2.4
Ill. 3		Marion	14561		
	330	" (a)	14335	226	—1.6
Ill. 9		Staunton	14615		
	91,92,93,94(a)	" (a)	13933[1]	682	—4.7
Ill. 10		West Frankfort	14647		
	364	" (b)	14332	315	—2.2
Ill. 14		E. of Springfield	14464		
	81,82	" (a)	14020[1]	444	—3.1
Ill. 15		Centralia	14587		
	167,168,169	" (b)	14257[1]	330	—2.3
Ill. 16		Herrin	14558		
	323,325	" (a)	14267[1]	291	—2.0
Ill. 18		La Salle	14722		
	393	" (b)	14440	282	—1.9

(a) Samples not from same mine, but from adjacent mines.
(b) Samples from the same mine.

In further testing this matter of age, fresh samples were collected by us for comparison with our own samples of 10 months' standing, and

[1] Average of several samples from neighboring mines.

calorimetric determinations made as before. Table No. 3 gives the results of this comparison, which showed that these new values are uniformly higher upon the fresh samples than upon the old. The variations lie between 1.3 per cent. and 3.4 per cent.

TABLE NO. 3.—COMPARISON OF VALUES FOR FRESH AND OLD SAMPLES BY ILLINOIS GEOLOGICAL SURVEY.

Ill. G. S. Lab. No.	Locality.	B T.U. per lb. ash, water and sulphur-free coal.	Difference in B.T.U.	Per cent. of difference in B.T.U.
421	DuQuoin, fresh	14386		
307,308,309	" old(*a*)	14009[1]	377	—2.6
460 and 1088	Herrin, fresh	14647		
323,325	" old(*a*)	14285[1]	362	—2.5
460	Clifford, fresh	14615		
325	" old(*b*)	14213	402	—2.7
462	Marion, fresh	14781		
330	" old(*b*)	14335	446	—3.0
540,740,741	Springfield, fresh	14468[1]		
81,82	" old(*a*)	14020[1]	448	—3.1
557	Westville, fresh	14550		
332	" old(*b*)	14054	496	—3.4
558	Himrod, fresh	14564		
333	" old(*b*)	14087	477	—3.3
1111	Eldorado, fresh	14857		
317	" old(*b*)	14597	278	—1.9
358	" old(*a*)	14662	195	—1.3
1114	Harrisburg, fresh	14931		
315	" old(*b*)	14622	309	—2.1
1110	3 miles E. of Eldorado, fresh	15131		
359	" " old(*b*)	14939	192	—1.3
1119	Maryville, fresh	14450		
418	" old(*b*)	14134	316	—2.2
1121	Norris City, fresh	14658		
316	" old(*b*)	14322	336	—2.3

(*a*) Samples not from same mine, but from adjacent mines.
(*b*) Samples from the same mine.

A third comparison was also made as between freshly collected and determined samples here and those made by the St. Louis Fuel Testing Plant; the results are given in Table No. 4. Here the differences are equally distributed between those of a plus and minus character. To determine, if possible, what effect the time element might have on these variations, the two extremes were selected and by correspondence, with the chemist of the Geological Survey at St. Louis, it was found that

[1] Average of several samples from neighboring mines.

Illinois No. 7, with an extreme variation of +1.7 per cent., showed its calorimetric value to have been determined upon the sample twenty days after collection at the face of the vein. Our own sample, which, as nearly as we could determine, was analyzed ten days after collection, showed a higher value as indicated. The other extreme, Illinois No. 9, with a drop in our results of —2.4 per cent., was found by the records of the Fuel Testing Plant, to have been but six days old. The exact age of our own sample is not definitely known, but it was not less than from ten to fifteen days old. The other variations are small and might be accounted for on other grounds than that of age of the sample.

TABLE NO. 4.—COMPARISON OF NEW U. S. G. S. SAMPLES WITH NEW SAMPLES OF THE ILL. STATE GEOL. SURV.

U. S. G. S. No.	Ill. S. G. S. Lab. No.	Locality.	B.T.U. per lb. ash, water and sulphur-free coal.	Difference in B.T.U.	Per cent. of difference in B.T.U.
Ill. 3		Marion	14561		
	462	" (b)	14781	+220	+1.5
Ill. 4		Troy	14439		
	1118	" (b)	14168	—271	—1.9
Ill. 7		Collinsville	14373		
	723,724,725	" (a)	14621[1]	+248	+1.7
Ill. 9		Staunton	14615		
	735,736,737	" (a)	14260[1]	—355	—2.4
Ill. 14		E. of Springfield	14464		
	540,740,741	" (a)	14468[1]	+ 4	+0.03
Ill. 16		Herrin	14558		
	459,460,1088	" (a)	14647[1]	+ 89	+0.6
Ill. 19		Zeigler	14601		
	419,420	" (b)	14463	—138	—0.9

(a) Samples not from same mine, but from adjacent mines.
(b) Samples from the same mine.

In Table No. 5, the average differences as between old and fresh samples by the two laboratories is assembled, and does not need explanation.

TABLE NO. 5.—AVERAGES OF TABLES NOS. 2, 3 AND 4.

17 Illinois Geological Survey samples compared with 8 United States Geological Survey samples	Average 365 B. T. U.
Illinois Geological Survey samples analyzed 6 months to 1 year after collection; United States Geological Survey analyses made soon after collection.	or 2.5 per cent. lower.
17 Illinois Geological Survey samples analyzed 6 months to 1 year after collection, compared with 16 similar samples analyzed within two weeks after collection.	Average 356 B. T. U. or 2.4 per cent. lower.
16 Illinois Geological Survey samples analyzed within 2 weeks after collection, compared with 7 United States Geological Survey samples analyzed soon after collection.	Average 29 B. T. U. or 0.2 per cent. lower.

[1] Average of several samples from neighboring mines,

It seems evident from these results that the drop in values occurs within the first two or three weeks after the coal is broken out of the seam, but the rapidity and extent as to any given length of time, is not easily determined and can be inferred only from such data as are found in the tables. Presumably, it is due in the main part to exudation of combustible gases consequent upon the releasing of the coal from conditions of pressure and sealing in the vein.

A second series of facts relates to a secondary process which undoubtedly begins after the breaking out of the coal from the seam, namely, the oxidation of compounds in the coal. This is, perhaps, more properly designated under the name of weathering. Advantage has been taken of the fact that in a number of mines, old pillars have been standing, and samples have been procured from these, after properly cleaning the surface, and comparing the results with samples obtained at the freshly worked faces of the mine. In Table No. 6 the results are given for such samples from pillars twenty-two and twenty-seven years old. The pillar coal shows a loss in comparison with the fresh coal of approximately 2.5 per cent. In the same table are given also the results for samples from another mine which have been subjected to various conditions, including submerging for one year, and the analysis of coal which has been exposed to the weather for one year. The difference is inappreciable as between the outer surface of the pile and that of the interior.

TABLE No. 6.

Test No.	Material.	B.T.U. per lb. referred to ash, water and sulphur-free.	Drop in heat units compared with initial values.
	Belleville, Illinois		
1	Fresh face sample	14785	
2	Pillar coal, 22 years exposure	14372	413
	Equality, Illinois		
3	Fresh face sample	15188	
4	Pillar coal, 27 years exposure	14754	434
	Westville, Illinois		
5	1¼ inch screenings 1 week from mine	14627	
6	3 inch nut, 1 week from mine	14586	
7	1¾ inch screenings, submerged 1 week after mining, for 1 year	14588	
8	From surface of 15 ton pile, 1 year exposure	14241	347
9	From throughout 15 ton pile, 1 year exposure	14264	324
10	Four weeks after mining	14410	178

Six other weathering tests have been conducted on smaller samples by Mr. N. D. Hamilton. Each sample was subjected to different conditions, namely, submerged; exposed to the weather; exposed to a dry

atmosphere, at a rather elevated temperature; and a duplicate of the latter with frequent drenchings with water. A charting of the results, which is more or less characteristic of all the tests, is given in Fig. 1,

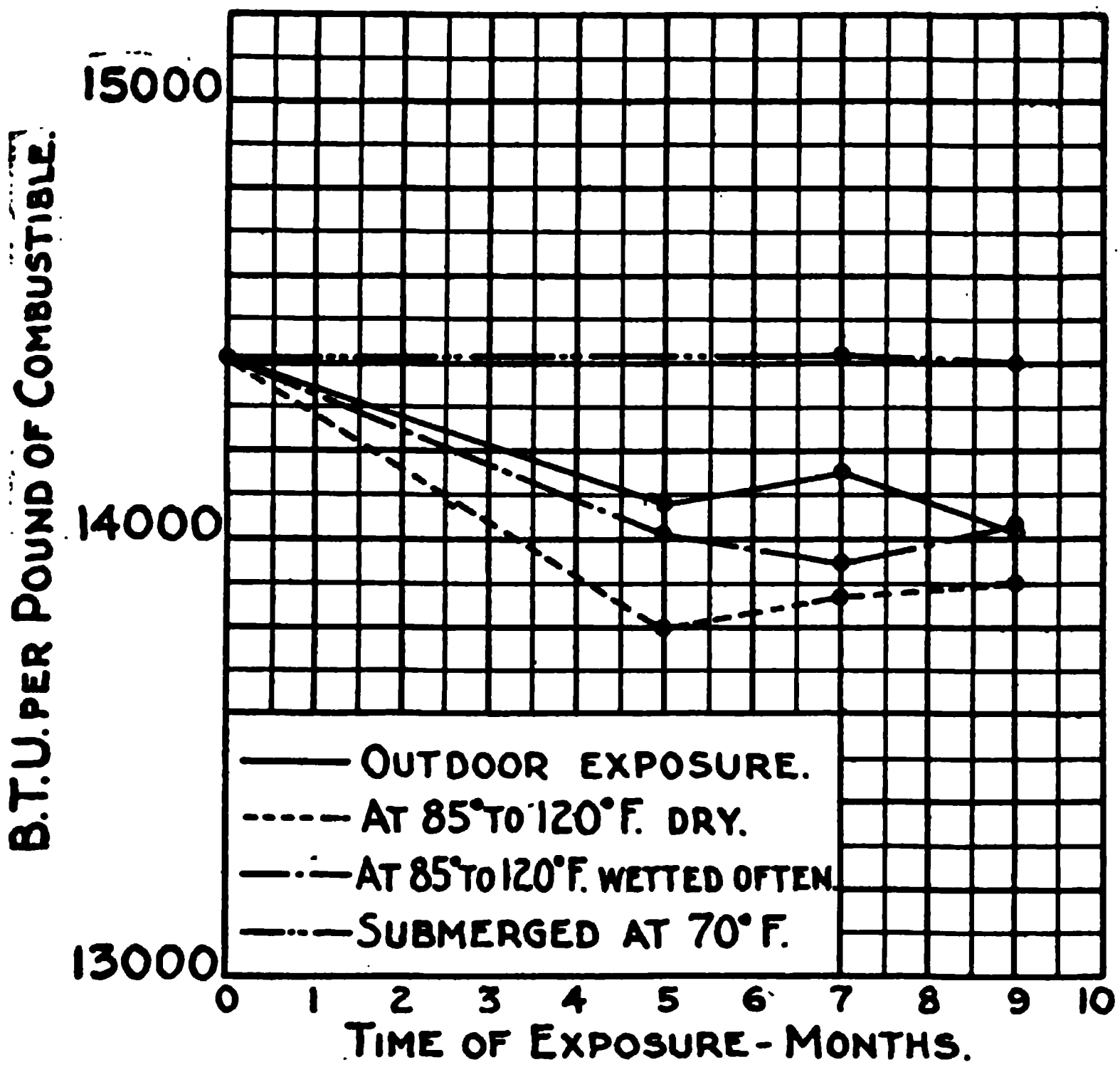

FIG. 1.

which is sufficiently clear to be self-explanatory. While the results of this series of tests are not conclusive, they point to the fact that submerged coal is without loss so far as oxidation processes are concerned; that exposure to a dry atmosphere is quite as conducive to the loss of heat values as exposure to weather and that, in general, these calorific losses are largely overestimated and probably, on an average, do not exceed 3 or 4 per cent. in amount.

A continuation of these tests upon carload lots is now being made under conditions of outdoor exposure, housing in bins, and in the submerged conditions, with some accompanying experiments intended to develop, if possible, the conditions which result in spontaneous combustion.

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STUDIES ON DIRECT NESSLERIZATION OF KJELDAHL DIGESTATES IN SEWAGE ANALYSIS.

By George O. Adams and Alfred W. Kimball.

Received April 10, 1908.

Of late much has been written concerning the great advantage of direct readings of Kjeldahl digestates over the distillation method. The greater accuracy of the method, the more simple technique, the less bulky and bothersome apparatus, and the great saving of time are among the chief advantages claimed for the method. To test the truth of these claims, a series of parallel determinations were made at the Lawrence Experiment Station under the direction of Mr. H. W. Clark.

Previous Methods.—Several procedures have previously been advanced, each one claiming to obtain satisfactory results under local conditions. Kimberly and Roberts[1] determine the total unoxidized nitrogen by adding nitrogen-free sulphuric acid to a measured amount of sewage and digesting until colorless. The digestate is transferred to a 50 cc. flask, cooled, and made up to the mark. Twenty-five cc. of this mixture are transferred to a 100 cc. flask, a 25 per cent. caustic soda solution added nearly to neutralization, cooled and more caustic soda added until a flocculent precipitate appears, when 2 cc. of a 10 per cent. sodium carbonate solution are added to precipitate the calcium present. The whole is then made up to 100 cc., shaken thoroughly, and allowed to stand six hours, when a portion of the supernatant liquid is pipetted into a 50 cc. Nessler tube, made up to 50 cc., nesslerized and read. They found it necessary to use caustic soda free from organic matter because otherwise turbid tubes were obtained.

Whipple[2] altered the procedure by diluting the digestate to 250 cc., treating an aliquot portion of this solution with an equal amount of 5 per cent. caustic soda solution, and substituting filtering through filter paper washed free from ammonia in place of the long period of settling. He found ordinary "purified stick" caustic soda caused no trouble from turbid tubes.

The Lawrence sewage is a strong domestic sewage low in calcium and magnesium content. It was therefore not necessary to consider the calcium in our experiments so no sodium carbonate was used. The method of Whipple was tried but did not give satisfactory results. The amount of free sulphuric acid present in the Kjeldahl digestate varies so that it is impossible to take an aliquot portion after dilution, add an equal amount of 5 per cent. caustic soda solution, and have anywhere near the same excess of caustic soda present in the different digestates.

[1] Kimberly and Roberts, *Jour. Infect. Dis.*, 1906, 2, p. 109.

[2] Whipple, *Tech. Quart.*, 1907, 162.

As a result of this difficulty a large number of turbid tubes were obtained, due to the presence of too large an excess of caustic soda.

Method.

To overcome this difficulty the following method was devised:

Reagents.—The same as those used in ordinary Kjeldahl determinations of organic nitrogen, with the addition of a 5 per cent. solution of caustic soda.

Method.—Fifty cc. of the sample (or more if the nitrogen content is low) are put in a Kjeldahl flask, diluted sodium carbonate added, and boiled down to about 20 cc. to remove the free ammonia. Then 5 cc. of nitrogen-free sulphuric acid (1.84) is added and the sample digested until colorless. The digestate is transferred to a 250 cc. flask, diluted to about 100 cc., and a 50 per cent. caustic soda solution added almost to neutralization. After cooling, a 5 per cent. solution of caustic soda is added in slight excess, the sample made up to 250 cc. and mixed thoroughly. This is filtered through a filter paper washed free from ammonia, 10 cc. of the filtrate are pipetted into a Nessler tube, made up to 50 cc. with ammonia-free water, mixed by shaking, nesslerized, and read after fifteen minutes.

Discussion.

Turbidity.—The Lawrence sewage being very low in calcium and magnesium content, the chief difficulty experienced from turbid tubes was due to the presence of too great an excess of caustic soda in the neutralized digestate. All tubes having an excess of less than 0.05 gram caustic soda in 50 cc. gave turbid tubes due to incomplete precipitation of magnesium. Most tubes having an excess greater than 0.20 gram in 50 cc. were also turbid. The excess of caustic soda must therefore be between 0.05 and 0.20 gram per tube to obtain clear tubes. Kimberly and Roberts say that if potassium permanganate is used to complete the digestion, turbid tubes will be obtained. Since the use of that salt is not necessary for completing the digestion of ordinary sewages, it is not used at this laboratory. In this laboratory a high-grade commercial caustic soda costing six cents per pound is used for all work and no difficulty was experienced from turbid tubes unless the excess of caustic was outside the limits above mentioned. The neutralization of the whole digestate rather than a small portion thereof reduces somewhat the correction due to the blank and the smaller portion taken for nesslerization allows of a greater excess of caustic in the whole digestate without causing turbid tubes.

Accuracy.—Of 90 parallel determinations, 65 per cent. of the direct determinations are lower, 32 per cent. are higher, and 3 per cent. the same as the distilled determinations.

COMPARISON OF RESULTS BY DISTILLATION AND DIRECT METHODS.

Kjeldahl Nitrogen (Organic), Parts per 100,000.

	Regular sewage.		Settled sewage.		Septic sewage.		Contact and trickling effls.	Sewage + 50% city water.
	Unfilt.	Filt.	Unfilt.	Filt.	Unfilt.	Filt.		
Number of samples....	13	11	13	13	6	5	24	5
Av. distilled.....	1.27	0.56	0.97	0.59	0.83	0.46	0.52	0.90
Av. direct.....	1.29	0.58	0.93	0.57	0.88	0.46	0.47	0.82
Max. difference.....	+0.22	+0.22	—0.30	+0.15	+0.10	+0.11	—0.19	—0.13
Min. difference.....	—0.01	+0.02	+0.01	0.00	0.00	—0.03	0.00	—0.02
Av. difference.....	+0.02	+0.02	—0.04	—0.02	+0.05	0.00	—0.05	—0.08
Av. % difference.....	1.6	3.6	4.1	3.4	6.2	0.0	9.6	8.9

Kimberly and Roberts, from 24 determinations, obtained results by the direct method, 41 per cent. of which were lower than the distilled, 33 per cent. higher, and 16 per cent. the same as the distilled determination.

Whipple in the same manner by the direct method, obtained 41 per cent. lower, 6 per cent. higher, and 53 per cent. the same as by the distillation method. From this it would seem as if the results obtained by the direct process are as a rule a little lower than they should be.

Time Necessary.—The chief advantage advanced for the direct method is the great saving of time accomplished by its use. That is to say, it can be done in less time by transferring the digestate to a flask, making up to a definite volume, mixing thoroughly, transferring an aliquot portion of this mixture to another flask, adding caustic soda almost to neutralization, cooling, then adding an excess of caustic soda, mixing thoroughly and either (1) allowing to stand for several hours, or (2) filtering through filter paper which must be washed free from ammonia, than by adding an excess of caustic soda and distilling two tubes.

In this laboratory there are eight stills available. It was found that if there were only four determinations to be made, the time required to distil the digestates was practically the same as by the direct method, but if there were more than four determinations to be made, by using the eight stills they could be done approximately twice as fast as by the direct method.

Furthermore, when the direct method is used, one's entire time must be directed to the digestates, whereas while distilling, something else may be done while the digestates are being distilled. This still further reduces the actual time of the distillation method as compared to the direct.

Apparatus and Technique.—While the direct method does away with the use of stills, on the other hand it makes necessary an increased handling of graduated flasks which are bothersome and bulky. It also calls for a large amount of nitrogen-free water which is a disadvantage, as

nitrogen-free water is not always available in large quantities in a sewage laboratory. In this laboratory two gallons and a half of nitrogen-free water can be made in about four and one-half hours. Starting with the water in the flasks cold, eight Kjeldahls can be distilled in about fifteen minutes. Figuring on this basis the cost of distilled water necessary for the direct method by Kimberly and Roberts' procedure is about one-fifth greater than by the distillation process, and by Whipple's procedure, about three times as great. If many determinations are to be made by the latter method the saving in the cost of water used would in a short time pay the cost of a still.

In the direct method the digestate has to be made up to volume at least twice and a definite amount measured twice, while in the distillation method but one measurement is necessary. The chance for error in manipulation is therefore four times as great by the direct as by the distillation method.

Conclusions.

The direct Kjeldahl method undoubtedly has its own place in sewage work, but it does not seem as if it should take the place of the distillation method in a permanent sewage laboratory handling many samples because of:

1. The greater amount of bothersome and bulky apparatus necessary.
2. The large amount of nitrogen-free water required.
3. The greater chance for error in manipulation.
4. The necessity of having the excess of caustic within narrow limits to avoid turbidity, this practically requiring a rough titration of each determination.
5. The greater length of time required for the determination.

The method, however, is without doubt an excellent substitute for the distillation method in a temporary laboratory where it is necessary to incur the least possible expense for apparatus or in a small laboratory where but a very few determinations are to be made daily.

LABORATORY OF THE LAWRENCE EXPERIMENT STATION,
LAWRENCE, MASS.

STUDIES OF INCUBATION TESTS.

BY H. W. CLARK AND GEORGE O. ADAMS.

Received April 10, 1908.

For the past seven years incubation tests have been made in the laboratories at the Lawrence Experiment Station to determine the stability of the effluents of contact and trickling filters. These studies have shown that the development of odor is, perhaps, the surest proof of putrescibility. Oxygen consumed and oxygen dissolved tests before and after incubation are of value but are sometimes contradictory. The so-called methylene-

blue test has been used to a considerable extent, but studies have shown that according to this test, some samples are putrescible, which, judging from the odor test only, are stable. In following out the work with this methylene-blue test, quite a number of dyes have been experimented with to find, if possible, one which would decolorize only when putrefaction as determined by odor, had also taken place. The dyes tested in this way were indigo carmine, methylene green, congo red, alizarin blue, acid brown, alkali blue, acid violet, aniline yellow, curcumein, ponceau red, martius yellow, methyl orange, tropaeolin, coccinine, toluidine blue and azo blue. Of these dyes, indigo carmine and methylene green are more readily decolorized than methylene blue, as will be shown later. Congo red, methyl orange and tropaeolin were the only others affected, but were too stable to use as an indicator of putrescibility in an incubation test. The results with indigo carmine and methylene green, however, looked promising enough to study.

During these studies, a test for hydrogen sulphide in the sample incubated, was made in connection with the other putrescibility tests. The test used is based on the formation of methylene blue from dimethyl-*p*-diamino-benzene sulphate in the presence of hydrochloric acid, hydrogen sulphide and ferric chloride, and by this method approximately 0.01 part of hydrogen sulphide per hundred thousand can readily be determined.

Samples of the effluents tested were incubated at 80° F. with methylene blue, methylene green and indigo carmine in bottles with tightly fitting stoppers, a blank being incubated at the same time. In each case enough dye was added to the sample tested to give it a decided color. The amount of dye used, however, within reasonable limits is not important, since samples with twice the amount of dye usually used were decolorized in the same period of time. Hydrogen sulphide was determined before and after incubation and the time required to decolorize the three dyes by incubation of the samples noted.

The procedure followed for the determination of hydrogen sulphide was as follows: Standards were made up in 100-cc. Nessler tubes from hydrogen sulphide water, the strength of which was determined by titration with iodine, and 2 cc. of strong hydrochloric acid containing $^1/_2$ per cent. ferric chloride and 1 cc. of a 1 per cent. solution of dimethyl-*p*-diamino-benzene sulphate. With small amounts of sulphide about thirty minutes are required for a good color to develop. Reagents were added to the proper amount of the samples to be tested, these samples being, also, in 100-cc. Nessler tubes and the colors developed in the samples compared with the standard colors. It was found that the same set of standards might be used for several weeks without change, and it was also found that equal amounts of reagents must be added to standards and to samples in order that the same shade of blue be obtained.

The following table shows the results of incubation of nineteen samples which did not putrefy. In these samples hydrogen sulphide did not form or odor develop, and with two exceptions, none of the three dyes was decolorized. Following this is a table showing the results of incubation of samples, all of which did putrefy.

TABLE SHOWING RESULTS OF INCUBATION OF NON-PUTRESCIBLE SAMPLES.

Effluent of Filter No.	Number of days incubated.	Hydrogen sulphide. Parts per 100,000. At start.	After incubation.	Methylene blue. Methylene green. Indigo carmine.	Appearance, odor, etc.
233	5	0.01	0.01	Not decolorized	No change
248	5	0.01	0.00	" "	" "
175	5	0.03	0.00	" "	" "
235	5	0.00	0.00	" "	" "
233	6	0.01	0.01	" "	" "
235	6	0.01	0.00	" "	" "
251[1]	6	0.01	0.01	" "	" "
136[1]	6	0.01	0.00	" "	" "
248	5	0.01	0.01	Decolorized in four days	Very slight increase in odor
251	6	0.00	0.00	Decolorized in four days	Very slight increase in odor
175	5	0.04	0.01	Not decolorized	No change
135	5	0.00	0.00	" "	" "
233	6	0.01	0.01	" "	" "
235	6	0.00	0.00	" "	" "
248	6	0.01	0.00	" "	" "
235	5	0.00	0.00	" "	" "
248	5	0.01	0.01	" "	" "
176	6	0.01	0.01	" "	" "
175	5	0.01	0.00	" "	" "

The results of the incubation of the 26 samples which may be said to have been putrescible are shown in the table on the next page.

Examining this second table, it will be noticed that in every case if one dye was decolorized the other two were also, and that the average time required for indigo carmine to be decolorized was 2 days; for methylene green, $2^1/_2$ days and for the methylene blue, nearly 4 days. In every sample tested after incubation there was an increase in the amount of hydrogen sulphide present, but no close relation could be noted between the amount of hydrogen sulphide formed and the appearance and odor after incubation.

It is probable that the hydrogen sulphide is largely formed from the decomposition of albuminous compounds in the effluents tested. Several samples shown in the above table were, as designated in the table, incubated with the addition of one part sulphur, as potassium sulphate,

[1] One part sulphur as potassium sulphate added before incubation, had no effect.

TABLE SHOWING RESULTS OF INCUBATION OF PUTRESCIBLE SAMPLES.

Effluent of filter No.	Days required to decolorize. Indigo carmine.	Methylene. Green.	Methylene. Blue.	Hydrogen sulphide. Start. Parts per 100,000.	After incubating. Days.	Hydrogen sulphide. Parts per 100,000.	Appearance.	Odor.
176	1½	2	5	0.03	5	0.40	sl. black	str.
176	1	1	2	0.01	2	0.05	....	d.
					5	0.10	....	d.
221	2	4	4		4		black	str.
221	2	1	3		3		black	str.
221	1	1	3		3		black	str.
221	1½	3	5	0.03	5	0.20	black	str.
221	¾	5	5	0.02	5	0.28	black	str.
221	2	4	4	0.05	4	0.25	black	str.
233	4	5	6		6		....	d.
233	5	4	6		6		....	d.
233	2	3	3	0.01	3	0.05	....	d.
247	2	2	4		4		black	str.
247	2	1	4		4		black	str.
247	1	¾	2		2		black	str.
247	1	¾	3		3		black	str.
247	1½	1½	5	0.02	5	0.80	sl. black	str.
247	¾	¾	¾	0.01	¾	0.06	....	str.
					5	0.30	black	str.
247	¾	3	3	0.01	3	0 25	black	str.
					5	0.25	black	str.
247	2	3	5	0.01	5	1.50	black	str.
247	3	4	4	0.02	4	0.35	black	str.
247	1	¾	3		3		black	str.
248	3	2	3		3		....	d.
251	3	¾	5	0.01	5	0.15	....	str.
251	3	4	6	0.01	6	0.20	....	d.
251	4	4	4	0.01	4	0.08	....	d.
					5	0.22	....	d.
251		Not decolorized		0.01	5	0.40	....	d.

and these showed no increase in the hydrogen sulphide formed above that formed in duplicate samples without the addition of the sulphate; on the other hand, a 1 per cent. solution of peptone in distilled water, seeded with one drop of sewage, developed 2.5 parts of hydrogen sulphide by five days' incubation. However, if putrefaction occurring is great, inorganic sulphates may be reduced as happened in the following experiment: Twelve bottles were filled with *sewage*. To six of them 1 part of sulphur as potassium sulphate, was added and incubated for one, two, three, four, seven and eight days, respectively. The hydrogen sulphide formed is shown in the following table, and it will be noticed that after three days' incubation there was a rapid development of hydrogen sulphide in the samples to which potassium sulphate had been added.

HYDROGEN SULPHIDE.
(Parts per 100,000).

Days incubated.	Sewage only.	Sewage + sulphate.
Start	0.00	0.00
1	0.04	0.04
2	0.10	0.10
3	0.30	0.35
4	0.35	1.20
7	0.10	2.50
8	0.10	2.50

One or two samples of filter effluents decolorized all of the dyes in four days without the production of hydrogen sulphide or odor, and, on the other hand, one sample showed a considerable development of hydrogen sulphide and odor without decolorizing in 7 days. These two or three results were, of course, abnormal and simply show that absolute reliance cannot be placed on incubation results obtained by the methylene-blue test; in fact, these studies have shown (1) that the degree of putrescibility of such effluents as experimented with can probably be better estimated by odor and appearance after incubation than by the time required to decolorize dyes; (2) the hydrogen sulphide formed comes very largely from albuminous compounds in the effluents and the amount formed is, to some degree, a measure of the putrescibility of the sample tested; (3) on the whole, it would seem that if a putrescibility test of the methylene blue kind is to be adopted, equally good results can be obtained in a shorter time by the use of indigo carmine or methylene green.

LABORATORY OF THE LAWRENCE EXPERIMENT STATION,
LAWRENCE, MASS.

NOTE.

The Quantitative Determination of Arsenic by the Gutzeit Method.—In the issue of *Chemical Abstracts* for April 10, 1908, p. 976, is an abstract of a note by T. F. Harvey on the estimation of arsenic by the Gutzeit test. As this immediately follows the abstract of an article by Sanger and Black on the quantitative determination of arsenic by the Gutzeit method, the casual reader may be led to infer that Sanger and Black were anticipated by Harvey in the method published by them.

I have already called the attention of the editor of the *Journal of the Society of Chemical Industry* to the misleading nature of Harvey's article, and Mr. Harvey himself has assured me that it is quite clear to him that his work had not come to our notice. The Harvey method, however, is merely a quantitative treatment of the ordinary Gutzeit test, while the paper of Sanger and Black not only introduces a different

principle into the procedure, but also includes a detailed study of the conditions of the reaction. CHARLES ROBERT SANGER.

HARVARD UNIVERSITY, CAMBRIDGE, MASS.,
April 30, 1908.

NEW BOOKS.

Lehrbuch der Gerichtlichen Chemie. BAUMERT, DENNSTEDT UND VOIGTLÄNDER. In zwei Banden. Zweite ganzlich umgearbeitete Auflage. 8°–xvi, 490. Braunschweig. F. Vieweg und Sohn. 1907. Price, 12 Marks, bound 13 Marks.

The first volume of the new edition of this manual by Dr. Baumert of the University of Halle is devoted to the detection and determination of poisons and noxious substances in the cadaver and excretions, in foods and beverages, household articles, water, air and soil and to chemico-legal problems in general. Volume II will be written by Drs. Dennstedt and Voigtländer, of Hamburg, and will be confined to the methods for the examination of inks, writings, signatures, forgeries, etc., and to the examination of blood, blood and spermatic stains and materials of a similar nature.

Dr. Baumert is entitled to the thanks and gratitude of analysts for having placed in their hands a manual of legal chemistry truly worthy of the name. Although a book of only 490 pages, it is a marvel of compactness and thoroughness. A reader, glancing over the table of contents, would be apt to form the opinion that the treatment, in general, must be incomplete, elementary and unsatisfactory, but upon careful study it becomes apparent that this is not true and that we have here one of those rare cases where an author has been able to do justice to his subject in remarkably few words, and that contrary to the verbosity of so many German writers we have in this book an exceptionally terse style.

While it is evident that the manual has been written to meet the needs of German chemists, the discussions are of such a nature and the reference to legal points and practice of such a character that it may be consulted with profit by all experts. At the present time this little book is unique in its field, being much more than a manual of determinative toxicology.

The author confines himself strictly to the chemistry of the materials discussed, all questions involving physiological effects, etc., being avoided so far as possible on the ground that such questions are not legitimately those of the chemist but rather of the medical expert, and that when the chemist has reported that in his judgment a substance is or is not present his work is done. Any subsequent questions as to whether the material found caused death, or could have caused death or was present contrary to law are not within the province of the chemico-legal expert.

The introduction is devoted to a very brief statement of fundamental facts relating to poisons and noxious substances, much space being

saved by avoiding any extended discussion, and by quoting from Kobert's "Kompendium." Following the introduction, three chapters, forty-nine pages in all, are devoted to the further presentation of general information for the guidance of analysts wishing to qualify as chemico-legal experts. For the beginner these pages are invaluable and even the experienced expert may read the suggestions of the author with profit, although the legal requirements of the German Empire are not deviated from. The suggestions made and facts here presented relate to such important topics as:

Chapter I. General rules to be followed in chemico-legal examinations; preliminary tests, planning the methods of analysis and the subsequent drawing up of reports and the statement of opinions; the laws governing the fees of experts in the German Empire. Chapter II. Poisonous materials found in foods, beverages, household articles, toys, etc., and finally in Chapter III, the author describes the methods for the testing and purification of reagents and apparatus in greater detail and more thoroughly than in any other manual of like scope with which the reviewer is familiar.

Part II, comprising the bulk of the volume, is devoted to the properties, methods of separation, identification and determination of such substances as the chemical expert may be called upon to search for. The common poisons are treated at length and as a rule in each case the methods given are many and varied, and the references to the original articles full, complete and down to date. Cross reference to other parts of the manual greatly facilitate the work of the analyst. If any comment may be made it is that possibly too great a choice is given, but this, on the whole, can scarcely be called an adverse criticism.

In the chapters devoted to inorganic substances in addition to the discussion of poisons, the legal questions arising concerning precious metals, their alloys, jewelry and counterfeit money are taken up.

An exceedingly valuable feature adopted by the author is to discuss in separate paragraphs under each substance treated, the materials in which the substance is to be found, the choice of methods to be employed and the general questions the chemist is called upon to answer. In these respects this manual is far in advance of any other. The methods of presentation and the nature of the information given may best be described by illustrations taken at random, for example. *Silver*—uses in the arts—forms met with in commerce—separation of silver from other elements—identification of silver—identification of silver compounds—determination of silver—the examination of hair, textiles, papers, etc., for silver—the recognition of silver stains—hair dyes, pharmaceutical silver preparations. *Phosphorus*—uses in arts—forms in commerce—poisoning by phosphorus—distribution in the cadaver—detection of phosphorus—

examination of the urine for phosphorus—identification of phosphorus compounds—determination of free phosphorus—analysis of commercial phosphorus—identification of phosphorous acid—phosphorus-containing compounds of commerce, matches, and methods for the study of match-making material and of the finished products with reference to the questions arising under the laws of the German Empire. Or take chapters of great interest at the present time to many American chemists, those devoted to sulphur dioxide and its salts, and to alcohol, here the sub-heads may be summarized as—*Sulphur dioxide*—general properties, identification, recognition in the air, examinations of foods for sulphites, determination of sulphites in wines, beer, etc., their detection in flesh, in fats—the identification and determination of sulphur dioxide in plants, the investigation and effects of flue gases, smelter fumes, etc.—and—*Alcohol*—properties, detection--determination--alcoholic beverages, analytical methods of German revenue service, the recognition of denatured and renatured alcohol—tables giving percentage composition of alcohols, etc.—detection of methyl alcohol in beverages, etc., amyl alcohol, etc., etc. It will be seen from these illustrations that the book is much more than a manual of chemical toxicology.

The chapters devoted to alkaloids, glucosides and other substances of vegetable origin are complete, down to date, and so well arranged that after glancing over the book one is able to find at once just the information one wishes both as to separation methods and identity tests. The color reactions are all tabulated and so arranged as to render consultation easy. Here again the analyst is given a variety of methods with the opinion of the author as to the choice under given conditions, an excellent system of cross references being introduced to aid in comparing the reactions given by different substances.

An excellent index covering both author's names and subject matter completes the book.

An appendix is devoted to such of the laws of the German Empire as the expert chemist must be familiar with and with a few tests and methods of investigation inadvertently omitted in the text. The book is so well written and the methods otherwise so judiciously chosen that it is a matter of surprise that the author makes so little use of the microscope, an instrument absolutely indispensable in chemico-legal examinations.

E. M. CHAMOT.

Benedikt-Ulzer, Analyse der Fette und Wachsarten. Fifth, revised edition, by FERDINAND ULZER, P. PASTROVICH AND A. EISENSTEIN. Large octavo, xiii + 1168 pages, 113 figures in text. Berlin: Julius Springer. 1908. Price, M. 26.50.

The first edition of Benedikt's Analyse der Fette appeared in 1886. Out of it have grown two monumental works which serve as the standard guides to the analysis of fats and waxes in the English and German lan-

guages. Since 1886 the progress in fat analysis and in the fats and oils industries has been astonishing, and the book under consideration bears striking evidences of this fact. In 1886 many of the physical and chemical methods for the examination of fats had been worked out in essentially the same form in which they are applied to-day. For example, the method of determining "titer," practically dates from Rüdorff's work in 1856; Reichert's value and Hehner's value date from 1879; Merz's acid number from 1880; Hübl's number and Köttstorfer's number from 1884. On the other hand, since 1886, have developed such important factors in this field as the acetyl number (1887); Hehner's method for the determination of glycerol (1889); Twitchell's method for the determination of rosin (1891); Wolfbauer's work on the "titer" test (1894); Twitchell's method of saponification (1898); Connheim's ferment method of saponification (1902); and many others. The edition of 1886 of Benedikt's work was scarcely one-fourth the size of the volume under consideration. Benedikt died in 1897, just before the third edition was published, and it speaks well for his care and foresight that the general plan of presentation has been followed from the first edition to the last. It is a most difficult matter to bring an old book up to date, but this has been done admirably in the present instance. The subject matter has been divided into two main divisions, the first (550 pages) devoted to the general analysis of fats and waxes and examination of technical products of the fat industries, the second (591 pages) covering the natural fats and waxes and their examination. The first part is written in collaboration with P. Pastrovitch, Director of the Oleomargarine, Candle and Soap Works, "Salvator" in Vienna; the second with A. Eisenstein, assistant in the Technological Industrial Museum in Vienna. The components of fats and waxes, chemical and physical properties, determination of physical constants and the qualitative and quantitative analysis of these substances and their impurities and unsaponifiable constituents and the by-products of the manufactures into which they enter, are treated at length. Methods of chemical control receive considerable attention. While the work is not primarily designed as a treatise on the technology of fats, the industries based on fats and waxes are entered into to a considerable extent. The descriptions of individual oils, fats and waxes are complete and adequate. Throughout the book, errors and misprints are very few. Footnote references are especially complete and the absence of footnote comments makes reading easy. The indexes are good and the typography, printing and paper all that could be desired. The work still stands as the best in German on the analysis of fats and waxes. W. D. RICHARDSON.

Detection of the Common Food Adulterants. By EDWIN M. BRUCE. New York: D. Van Nostrand Co. 1907. Cloth, 12mo. vii + 84 pp.

This little book has been prepared by the author as a simple qualitative manual for food inspectors, and for teachers and students of chemistry.

The qualitative tests presented, comprise, with a few additions, the principal ones given in Bulletin No. 65, of the Bureau of Chemistry, U. S. Department of Agriculture, and in Leach's "Food Inspection and Analysis." Frequently, the descriptive language has been condensed. While brief introductory notes are given stating the principal adulterants to be found in the several classes of foods treated in the respective chapters, there are few cautionary and explanatory notes—a defect in a text for beginners in this field of applied chemistry. At a few points, the work is not up to date. Thus, in speaking of the doubledyeing test, on page 35, the author states that "nothing but coal-tar will color in this second dyeing;" whereas, it is now well known that lichen dyes also possess this power. The chapter on honey does not mention the newer tests for invert sugar. The book will doubtless, however, serve well the purpose for which it was written. There is a good general index and an index of tests by authors, so that convenience of reference is secured.

WM. FREAR.

Medico-Physical Works, being a translation of *Tractatus quinque medico-physici* by JOHN MAYOW. Alembic Club Reprints, No 17. Chicago: The University of Chicago Press. 1908. pp. xxiii + 331. Price, $1.36, post-paid.

"How true it is that the value of truth is not absolute; there is a time and place for everything, including a new truth. If a discovery is made before its time, it withers up barren, without progeny, as did Mayow's." Thus wrote Sir Michael Foster in his lectures on the history of physiology. It is astonishing to learn how adequately some of our present views on chemistry and physiology are foretold in the writings of Mayow, whose observations were allowed to remain unappreciated for nearly a century and until Lavoisier had contributed his researches on oxidation. The existence and functions of oxygen were foreshadowed in Mayow's nitro-aërial spirit which he recognized as that part of the atmosphere which supports combustion; it is present in nitre and enters the blood in respiration. With a few verbal changes Mayow's description of the mechanism of respiration might serve as a text-book account of the physical features of the process to-day. The fundamental characteristics of muscular metabolism were also clearly appreciated, and that at a time when the nature of gases was obscure. "We may then suppose," wrote Mayow, physiologist and chemist, in the essay on respiration (1668), "that nitro-saline particles (*i. e.*, oxygen) derived from the inspired air constitute the one kind of motive particles, and that these, when they meet the others, the saline-sulphurous particles (*i. e.*, combustible substances) supplied by the mass of the blood and residing in the motor parts, produce the effervescence from which muscular contraction results" (p. 208).

If the discussions on animal spirits, which Mayow identified with his nitro-aërial particles, are less suggestive to-day, they are none the less interesting as a record of contemporary chemical and physiological progress. As a specimen of these early views the following quotation is of interest: "If the stomach be quite empty of food, its internal membranes are, as is probable, pinched by the nitro-aërial particles, and hunger seems to arise from this."

It is a pleasure to have a thoroughly readable English translation of these classic papers by Mayow. They can be recommended as entertaining specimens of scientific imagination and critical acumen, as well as striking illustrations of an appreciation of the experimental method long before the modern period of discovery in chemistry.

LAFAYETTE B. MENDEL.

Descriptive Biochemie mit besonderer Berücksichtigung der chemischen Arbeitsmethoden. By DR. SIGMUND FRÄNKEL. Dozent f. med. Chemie an der Wiener Universität, Wiesbaden: J. F. Bergmann. 1907. pp. 639. Price, 17 Marks.

This book contains a description of the substances occurring in the animal body together with the methods for their isolation, their synthesis, and their quantitative determination and also their degradation products. Special chapters are devoted to the ferments and to the chemistry of the organs, secretions and excretions. The book is intended to serve as an aid to workers in physiological chemistry. In the preparation of the book, the literature up to the end of the year 1907 was consulted and numerous citations are made.

The facts of physiological chemistry are given in the book in the most compact sort of way but not to the detriment of the subject. Some exception, however, may be taken to the very free use made of abbreviations of names of common things which will require the reader to learn quite a number of abbreviations devised by Fränkel himself. In some parts of the book there appears evidence of haste in the preparation of the manuscript as shown by inaccuracies of statement and incorrect formulas. The book contains a vast amount of valuable information brought up to practically the latest date, and is a rich mine to physiological chemists.

JOHN MARSHALL.

Studies in Plant and Organic Chemistry and Literary Papers. By HELEN ABBOTT MICHAEL (Helen C. DeS. Abbott), with Biographical Sketch. Cambridge, Mass.: The Riverside Press. One vol., pp. 423. 1907. Price, $2.50 net.

Although the subject of this appreciation had a "genius" for music she deserted it to study Helmholtz's work on optics. From physics her "interest ran to zoology and the dissecting of animals." Next she enters a medical college and passes "the first year's examination in chemistry, anatomy and physiology with a record of one hundred in

each branch." Her investigative turn of mind then finds expression in working out several phytochemical problems and in delivering public lectures on such broad subjects as "plant analysis as an applied science," "the chemical basis of plant forms," etc.

Not content with what she can attain on this side of the Atlantic, she goes to Europe in search of a laboratory in which to pursue her phytochemical studies. However, she returns to America and resumes the study of medicine. After her marriage she starts on a trip around the world. A short residence at Worcester is soon interrupted and residence is taken up in the Isle of Wight where a private chemical laboratory is equipped. Here she works jointly with John Jeanprêtre as she had previously worked with Trimble in Philadelphia.

Returning once more to America she delivers her last lecture on a phytochemical subject. Again she goes abroad, but this time "her interests" are "enlisted in wider fields," *i. e.*, she writes about the Austrian peasant and kindred topics. A third time she matriculates at Tufft's and wins her medical degree in 1903. After a short medical practice she died November 29, 1904.

EDWARD KREMERS.

Life and Scientific Activity of N. A. Menshutkin. By N. MENSHUTKIN. Published by M. Frolovaia, 6 Galernaia Street, St. Petersburg (In Russian).

A detailed biography and review of the work of the late N. A. Menshutkin by his son. Considerable space is devoted to telling of the struggles of the Russian students for liberty of assembly, etc., and of the faculties of the University and Polytechnic Institute for autonomy.

H. M. GORDIN.

Neue Capillar- und Capillaranalytische Untersuchungen. By FRIEDRICH GOPPELSROEDER. Basel: Emil Birkhauser. pp. xiv + 81 pp. + 52 tables. Price, 6 Marks.

This interesting little book is a concise report of original work in a field which the author has made peculiarly his own. He gives a list of his eight earlier publications upon the same subject, the first of which appeared in 1861.

As the facts Goppelsroeder has based so much work upon are, perhaps, not widely known, it may not be amiss to state them briefly. When strips of filter paper (cotton, linen or other fabrics may be used, but filter paper is generally preferable) are hung with their ends dipping in liquids or in solutions, capillary force causes the liquids to creep upward to definite heights which are different for different substances, as in capillary tubes. The effects of adsorption are also apparent and the result, when several substances are in the solution, is the formation of bands or zones of different widths, each zone containing mainly some one of the dissolved substances. Numerous qualitative separations can be brought about in this way, and corroborative color tests can be applied to the several bands on the paper.

The eighty pages of text seem brief for the amount of fact they contain and a stupendous number of separate observations are condensed into the fifty-two tables, some of which are large, opening out like maps. The following are some of the titles of chapters:

I. The effect of different kinds of filter paper upon the height to which liquids ascend.....IV. The effect of the length of paper immersed on the height to which liquids ascend.....VII. Influence on the ascension of a mordant action on the fibers.....VIII. Capillary analysis of the extracts from separate zones which were obtained by a preliminary capillary analysis....IX. Sensitiveness of capillary analysis.....X. Capillary analytical tests of water solutions of alkaloids.....XI. Capillary experiments with members of different homologous series of organic substances..... XII. Capillary experiments with water solutions of inorganic salts..... XIV. Capillary experiments with milk, with skimmed milk and with each diluted.

In some cases the results are gratifying, for instance potassium bichromate—sulphuric acid gave a positive test for strychnine on the filter paper strip when only one part of strychnine was present in 1,600,000 of the solution, while the same reagents did not detect one part of strychnine in 25,000 in the solution itself. Similar results were obtained with other alkaloids. In other cases the results are not so satisfactory. For instance, in one hour, pure milk rose 14.1 cm., diluted with 10 per cent. water it rose 14.7 cm., and diluted with 20 per cent. water it rose 16.4 cm. The difference in these heights is enough to make one hopeful but hardly enough to justify much reliance on the method for detecting watered milk. Capillary analysis in its present stage of development is an art rather than a science.

There is much of value to analysts in the book and it certainly should be in every reference library. S. LAWRENCE BIGELOW.

A Course of Practical Organic Chemistry. By T. SLATER PRICE, D.Sc., Ph.D., F.I.C., AND DOUGLAS TWISS, M.Sc., A.I.C. London: Longmans, Green & Co. 1907. xiii + 239 pp. Price, $1.20.

Both authors are connected with the Chemical Department of the Birmingham Municipal Technical School, Dr. Price being the head of the department and Mr. Twiss one of the lecturers.

The occasion for publishing the book, and the field it aims to fill are set forth in the preface as follows: "The recent revision of the Board of Education syllabus for Practical Organic Chemistry.....has naturally created the necessity for a text book which will cover the complete syllabus..... The present book really consists of an amplification of the notes which have been given to our own students.....who comprise (1) those working for the Board of Education examinations, and (2) for the B.Sc. degree," the classes being, "with few exceptions, held only in the evening."

The subject matter is divided into three Parts or Stages, corresponding presumably with those of the Board of Education syllabus, Stage I apparently covering Fatty Chemistry, and Stages II and III, Aromatic. Each of these stages is further subdivided into chapters, the contents of which appear to have been decided by genetic rather than by structural considerations.

It is, of course, a difficult matter for one not thoroughly familiar with the local conditions which this book aims to meet, to pass judgment upon how well it is likely to fulfil its mission. It is designed primarily to enable students to pass certain fixed examinations, and only those on the ground can tell how well it is succeeding.

As a laboratory text-book of organic chemistry for students in this country, it cannot be recommended. The style is too much that of the "cook book" type, and in the arrangement of the matter, representatives of widely different classes of compounds are grouped together because they happen to be obtained from the same substance. Formic acid, for this reason, appears in the chapter on bibasic acids. In several cases, the preparation of a substance is given in one part of the book and its characteristic tests and reactions in quite another. Many pages are devoted to separations of a special list of selected organic compounds, the scheme for which is given in detail.

A laboratory text-book should be something more than a collection of preparations. It should be so arranged as to be a useful adjunct to the lecture work, illustrating by practical examples the methods of preparation and classes of compounds discussed in the lecture course. In a subject of such limitless detail as organic chemistry, it is very important that the basis of classification should appear clearly in any laboratory book, so that the student should see this at once by the preparations given. The reviewer is also of the opinion that the working out of elaborate schemes for identifying one of a limited group of compounds, or separating a mixture of several of them, is undesirable from many points of view. The student should be taught the fundamental tests and reactions upon which all this depends, and then work out his own scheme of identification or separation, advancing from simple to more complex mixtures. This stimulates his interest, sharpens his powers of observation, and develops self-reliance, while the following out of a scheme devised by somebody else to cover a limited number of substances does not give him the same chance to test his own strength.

The student working through the book will, to be sure, gain a very good practical knowledge of the more important methods of preparing organic compounds, as well as an intimate acquaintance with a considerable number of typical organic substances, but if taken up in the order given, he will find it necessary to re-assort this information quite extensively before it

will run parallel to any of the lines of classification along which the subject of organic chemistry is generally developed.

As stated before, however, since the book aims to cover only a special field and is designed primarily for "home consumption," the above criticisms should not be construed too harshly. There are, on the other hand, many excellent features. The preparations selected are typical, the details are given clearly, and much more space is properly accorded characteristic reactions and analytical tests than is customary in such books. The book is in attractive form, and the proof has evidently been read with great care.

MARSTON TAYLOR BOGERT.

Practical Methods for the Iron and Steel Works Chemist. By J. K. HEESS, PH.C., Chief Chemist for the Carnegie Steel Company, New Castle, Pa. pp. 60. Easton, Pa.: The Chemical Publishing Co. 1908. Price, $1.00.

The author has compiled from various sources, methods for the analysis of such materials as iron ores, coke, coal, slags, irons and steels, firebricks, cements, boiler waters, fats, bearing metals, and chimney and producer gases. These have been modified to conform to his experience and it is stated that all procedures have been carefully tested, and that the directions as given are intended particularly as a guide to analysts of limited experience. For such readers the author also describes some of the essential features of a works laboratory, and gives directions for the general conduct of laboratory work, the preparation of reagents, or standards, and adds a collection of useful tables.

In his endeavor to make this a "practical" manual, the author has made his directions so concise as to approach, if not to pass, the danger point, especially in a work designed for inexperienced analysts. The volume is of interest as an expression of opinion on the part of one who is familiar with the demands made upon the laboratory of an iron or steel works, regarding methods best adapted for use in such a laboratory.

H. P. TALBOT.

A Laboratory Outline for Determinations in Quantitative Chemical Analysis. By ALBERT F. GILMAN, S.B., A.M., Professor of Chemistry, Ripon College. pp. 88. Easton, Pa: The Chemical Publishing Company. 1908. Price, 90 cents.

The procedures described include a considerable range of gravimetric analyses and the volumetric determination of iron by the permanganate, dichromate, and stannous chloride methods. Each procedure is accompanied by a series of questions to be answered by the student, and a page upon which it is apparently intended that the student shall record his observed data.

It is, unfortunately, impossible to commend this little volume. It is badly written, the procedures are not accurately described, and many of them are unreliable, as the author states with singular frankness but

without excuse for their presentation. The number of typographical errors is not creditable to either the author or the publishers.

H. P. TALBOT.

Analysis of Mixed Paints, Color Pigments, and Varnishes. By CLIFFORD DYER HOLLEY and E. F. LADD. John Wiley & Sons, New York. Price, $2.50.

Prof. Ladd's contribution to the present volume is a dissertation on Mixed Paints in general, with particular reference to their truthful labeling and to the experience of North Dakota in legislation to compel such labeling. In his discussion of this matter, he is fair and his arguments are convincing.

Part II of the book upon the analysis and testing of paints, by Prof. Holley, treats of the subjects from the standpoint of one who has recently been called upon to analyze a great number of the paints, both good and bad, that are now on the market. The discussion and the methods of analysis recommended, are more complete and satisfactory when pigments are dealt with than in the case of the vehicles. It may be said with fairness, that this is the best work that has yet appeared on the analysis of the pigments of the present day.

A chapter is devoted to the Practical Testing of Paints. This most important subject has been taken up by the North Dakota Government Experiment Station, and an account is given here of their methods of operating.

The book is certainly of value to all who are interested in the subject.

PARKER C. MCILHINEY.

Commercial Organic Analysis. By ALFRED H. ALLEN, F.I.C., F.C.S. Vol. II-Part III. Third Edition. Revised by the Author and Arnold Rowsby Tankard, F.C.S. P. Blakiston's Son & Co., Philadelphia. 8vo. 547 pp. Price, $5.00.

A comparison of the present book with the parts of the former edition which related to the same subjects, brings out forcibly the fact that upon these branches of analytical chemistry, a tremendous amount of work has been done in the interval between the two editions. The subjects treated are, The Aromatic Acids, Resins, and Volatile or Essential Oils. The statement on the cover, that the subject of Phenols is also treated, is misleading; this subject is really treated in Part II of Volume II.

There is, inevitably, in the discussion of such subjects as those to which this book is devoted, a certain lack of connection or logical sequence between its several parts. The properties, uses and analytical necessities of such materials as organic acids, resins and essential oils vary so greatly among themselves that a systematic or connected treatment of their analytical chemistry is a very difficult task. The present work is not faultless in this respect, but the great amount of information contained, makes up for its somewhat disjointed composition. The work

of bringing up to date the various subjects discussed, has in the main been well done. PARKER C. MCILHINEY.

Chemical Reagents, their purity and tests; a new and improved test based on and replacing the latest edition of Krauch's "Die Prüfung der chemischen Reagentien auf Reinheit." By E. MERCK. Authorized translation by Henry Schenck, A.B. (Harvard). New York: D. Van Nostrand Company. 1907. vii + 250 pp. Price, $1.50 net.

It would be superfluous to describe the arrangement and treatment of subjects in Krauch's well-known book. The English translation is from the fourth edition, which was published in 1905, and it is to be noted that no literature references of a later date are given. German idioms are conspicuously absent, and for this novelty (as we may fairly say) as well as for his uniformly clear phraseology, the translator is to be commended. In the main, also, he adheres to the chemical terminology and spelling which are at present, adopted by the leading American and English journals, but which so many chemists still disregard or are ignorant of. We refer more particularly to the endings—in, -ine and -ol. As, hematoxylin, iodeosin (but eosine is given on page 88), hematein and phenolphthalein, all of which are non-basic; but brucine, diphenylamine and aniline which are basic. His usage in regard to -ol, is not quite so uniform. Pyrogallol and resorcinol are correctly given, with the older names in parenthesis, but glycerin is preferred to glycerol (given in parenthesis). So, also, phloroglucin and furfural (furfurol)—for furol—are given. But all these points are, no doubt, of minor importance and detract little from the value of the book. The tests given are certainly delicate enough for all but the most critical work, and with this qualification, the book can be recommended to all chemists. It is not too much to hope that in some future edition of this or of a similar work, even more delicate tests, which will satisfy the demands of the highest accuracy, will be given for at least the commoner reagents. C. E. WATERS.

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